

R&D 9185-MS-02

68171-01-M-6166

**VI International Symposium  
on Self-Propagating High-Temperature Synthesis  
(SHS-2001)**

*Technion, Haifa, Israel  
February 17-21, 2002*

**BOOK OF ABSTRACTS**



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**The Symposium SHS – 2001 was supported by:**

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***Department of Materials Eng., Ben Gurion University***

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<p><b>1. REPORT IDENTIFYING INFORMATION</b></p> <p><b>A. ORIGINATING AGENCY</b> Technion, Haifa, Israel</p> <p><b>B. REPORT TITLE AND/OR NUMBER</b> VTP Report Series VTP-1000-2002. Proceedings</p> <p><b>C. MONITOR REPORT NUMBER</b> R-0185-19502</p> <p><b>D. PREPARED UNDER CONTRACT NUMBER</b> N6171-01-0-616</p> <p><b>2. DISTRIBUTION STATEMENT</b></p> <p><b>APPROVED FOR PUBLIC DISTRIBUTION</b></p> <p><b>DISTRIBUTION UNLIMITED</b></p> <p><b>PROCEEDINGS</b></p>		
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## PREFACE

This is the book of abstracts of invited lectures, mini-reviews, oral and poster presentations included in the Program of the VI International Symposium on Self-Propagating High-Temperature Synthesis (SHS-2001).

Invited Lectures by F. Aldinger (Nanocrystalline Ceramics by Solid State Thermolysis of Metalorganic Polymers), R. Brook (Trends in Ceramic Materials Development into the Third Millennium), R. Tenne (Inorganic Nanotubes and Inorganic Fullerene-like Materials from Layered Compounds: Synthesis, Properties and Applications) and R.W. Cahn (Contaminants, Additives and Dopants in Modern Materials Science) are dedicated to general problems of modern materials science rather than to particular problems of SHS. No doubt, these lectures will give rise to new ideas in the SHS community.

Mini-reviews by J. Puszynski (Kinetics and Thermodynamics of SHS Reactions), Yu. M. Maximov (SHS in Electric and Magnetic Fields), F. Bernard (Mechanical Alloying in SHS Research), Sheng Yin (SHS-Produced Composite Materials) summarize the most recent achievements of modern SHS (research in the fields of experimental diagnostics, theory and mathematical modeling, chemical synthesis/technology, and advanced materials, respectively).

Key-note presentations by N. Claussen (Reactive Casting of Ceramic Composites), C.C. Ge (Present Status and Trends of SHS FGM), B.J. Matkowsky (On the Dynamics of Hot Spots in SHS Wave Propagation), R. Pampuch and J. Lis (SHS-Synthesis of Complex Ceramic Materials and Their Properties), E.N. Rumanov (Critical Phenomena at Autowave Propagation), K.G. Shkadinskii (Mutual Interdependence between SHS Reaction and Gas Infiltration during Thermal Explosion), A.S. Shteinberg (Electrothermal Explosion (ETE) Method to Study the Kinetics of Fast High-Temperature Reactions in Condensed Systems), Run-Zhang Yuan (SHS of TiB<sub>2</sub>-Based Multiphase Ceramics and Composites) present the authors' own accomplishments in the corresponding areas of SHS research.

Contributed papers (oral and poster presentations) that form the major part of the Symposium Program demonstrate the progress made in different directions of modern SHS research and development over the past few years.

Reports on experimental investigation and mathematical modeling cover the features of combustion in heterogeneous systems with a special emphasis on the role of the accompanying physicochemical processes. Besides the general, formalized combustion models, the program also includes reports on mathematical modeling of specific SHS processes. The Symposium Program also reflects the growing interest in the thermal explosion mode of SHS - a process especially promising in the case of low caloric reactions. Special attention is given to the role of the medium heterogeneity, phase transitions, and thermal explosion in the post-induction period (important for synthetic applications).

Traditionally, much attention is given to chemical synthesis and technology of ceramics (AlN,  $\alpha$ -Si<sub>3</sub>N<sub>4</sub>, SiC, SIALONs), intermetallics (Ni-Al, Fe-Al, *etc.*), and

complex oxides. New complicated syntheses recently performed in various inorganic and organic systems demonstrate the versatility and universality of SHS chemistry.

Phase and structure formation in combustion products is being investigated by time-resolved X-ray diffraction (using either synchrotron radiation or X-rays) and quenching - techniques that have become conventional by now.

As always, much attention is being given to technology and materials. The feasibility of existing SHS methods for the production of composite, functionally graded, cast, welded, coated, etc. materials and products has been confirmed. Reported are some new applications of SHS materials and products that are dictated by their specific properties. SHS methods are gradually penetrating into a new, rapidly developing area of nanophase materials.

A promising direction of research is the effect of shock waves on SHS. Besides clear technological application, of considerable interest are the attempts to observe the so-called gasless detonation predicted theoretically, but still not confirmed experimentally.

SHS in strong external fields (electric, magnetic, electromagnetic) is also included in the Symposium Program. These works are characterized by gradual shift from the basic to applied research (synthetic applications).

SHS in centrifuges is a traditional direction of research that has already found its practical application.

The Program also includes four Round Table discussions:

V. V. Barzykin, I. Gotman      *Thermal Explosion*

A. S. Rogachev      *Phase and Structure Transformations in SHS Processes*

I. P. Borovinskaya, R. Pampuch      *SHS Ceramics: Synthesis and Application*

V. I. Yukhvid      *Gravitational SHS Technology*

The Symposium Program and Book of Abstracts gives a clear picture of the state-of-the-art in modern SHS research and development. The Program includes about 160 presentations from 15 countries.

It is our hope that this book will be read not only by the SHS-2001 Symposium participants, but will also be interesting for a broader scientific community and will attract young researchers to the exciting field of Self-propagating High-temperature Synthesis.

Alexander E. Sytschev

Coordinator SHS'2001

## PLENARY AND INVITED LECTURES

### IL-3-220: Nanocrystalline Ceramics by Solid State Thermolysis of Metalorganic Polymers

**Fritz Aldinger, André Zimmermann**

*Max-Planck-Institut für Metallforschung and Institut für Nichtmetallische Anorganische Materialien*

*Universität Stuttgart Pulvermetallurgisches Laboratorium*

*Heisenbergstraße 5, D-70569 Stuttgart, Germany*

The condensation of preceramic compounds by solid state thermolysis is a fairly new process of producing novel types of ceramics. The general idea behind this process route is that molecules of metalorganic polymers already contain structural units of the inorganic materials, which are created by the condensation reactions during heat treatment, thus providing novel paths of controlling composition, atomic array and microstructure of ceramics. Conventionally as-thermolysed materials are amorphous and reveal glass-type near-range ordered structures, which could be crystallised by further heat treatment at higher temperatures into stable or metastable phases. Of special interest are covalent bonded inorganics on the basis of silicon, boron, carbon and nitrogen condensed out of proper siliconorganic polymers for high-temperature materials. Since with materials of this type devitrification of the amorphous state occurs at rather high temperatures quite stable nanocrystalline microstructures can be formed.

Both amorphous and crystalline precursor-derived Si-B-C-N ceramics create substantial interest, since they provide thermal stability, oxidation resistance and very attractive mechanical properties up to rather high temperatures.

### IL-1-211: Trends in Ceramic Materials Development into the Third Millennium

**Richard Brook**

*Oxford University, UK*

Even if ceramics are the materials with the longest technological history extending over several millennia, it is clear that recent decades have brought spectacular advances. Future materials developments will bring further exciting progress in compositions and in processing; the largest changes are, however, to be expected in the ways in which we use them – in their integration into larger systems, into the function of these systems, in the character of world commerce and in the changing challenges which we as individuals and as societies face. If we are to make real advances, we shall have to be able to see the wider picture.

### PL-1-210: SHS of Dense *in situ* Composites via Pressure Assisted Thermal Explosion: experiment and modeling

**E.Y. Gutmanas**

*Faculty of Materials Engineering, Technion, Haifa 32000, Israel*

Over the past decade, there has been a pronounced increase in SHS-related research activities in Israel. Both fundamental and applied aspects of SHS in its different modes are currently under investigation at major Israeli universities, research centers and research 'incubators' ('hamamot'). Along with the development of the science base of combustion wave propagation laid by Prof. A.G. Merzhanov and his colleagues, Israeli scientists direct their efforts towards the traditionally less investigated thermal explosion mode of SHS. A gradual shift from basic to applied research

has lead to the development of a variety of unconventional SHS processes such as thermal explosion in constrained dies under pressure, short distance reactive infiltration and reactive forging. These pressure-assisted combustion technologies are unique SHS processes that allow simultaneous synthesis and full density consolidation of single-phase and composite materials, which is the ultimate goal of combustion synthesis. Due to these processes' complexity, a special emphasis is given to experimental and computational modeling describing the synergetic effect of system dispersity/inhomogeneity and heat/mass transfer on the ignition and course of a self-sustained reaction under far-from-the-adiabatic conditions. Another field of SHS-related research activity in Israel is design and processing of advanced materials with smartly engineered microstructures such as functionally graded materials, machinable ternary carbides and nitrides and interpenetrating phase composites. One of the important research directions is investigation of the possibility of transforming waste materials (e.g. electric power stations coal waste) into useful products via SHS. Realization of the considerable promise of SHS as an energy-saving recycling tool could significantly contribute to the improvement of our ecology.

#### **IL-4-221: Contaminants, Additives and Dopants in Modern Materials Science**

**R. W. Cahn**

*Department of Materials Science and Metallurgy, Cambridge University, UK*

One of the defining features of the evolution of Materials Science and Engineering is the gradually dawning recognition of the central role of trace elements in governing the behaviour of materials. As this came to be recognized, so was the value of extreme purification of materials, as a precursor to the intentional addition of trace elements. Dirt (or an impurity) is simply matter in the wrong place, and correspondingly a dopant or additive is matter in the right place. The introduction of the electron microprobe analyser, the century's most important instrumental innovation, focused attention away from the mere concentration of a dopant to its microstructural location, segregated to grain boundaries in particular.

The lecture will include a number of exemplifications of these broad principles, in metallurgy, semiconductors and electroceramics particularly.

#### **IL-2-21 9: Inorganic Nanotubes and Inorganic Fullerene-like Materials from Layered Compounds: synthesis, properties and applications**

**R. Tenne**

*Department of Materials and Interfaces, Weizman Institute  
Rehovot 76100, Israel*

We have proposed that nanoparticles of layered compounds will be unstable against folding and close into fullerene-like structures and nanotubes (IF). Initially this hypothesis was realized in WS<sub>2</sub> and MoS<sub>2</sub>. Subsequently, nanotubes and fullerelene-like structures were prepared from numerous compounds of 2D habit. Much progress has been achieved in the synthesis of organic nanotubes and fullerene-like nanoparticles of WS<sub>2</sub> and MoS<sub>2</sub> and many other metal dihalocogenides over last year or two. Synthetic methods for production of multiwall WS<sub>2</sub> nanotubes by sulfidizing WO<sub>3</sub> particles have been described and further progress is underway. A fluidized bed reactor for the synthesis of 40-50g of fullerene-like WS<sub>2</sub> nanoparticles has been established and reported. The detailed mechanisms for the synthesis of fullerene-like WS<sub>2</sub> and MoS<sub>2</sub> nanoparticles and nanotubes of these compounds have been elucidated. Single wall MoS<sub>2</sub> and nanoparticles of MoS<sub>2</sub> were reported recently.

Substantial progress has been achieved in the use of such nanoparticles for self-lubricating mechanical parts. It was shown that impregnation of 3-8 wt% of these nanoparticles in various

porous matrices produced self-lubricating parts with a reduced friction, a higher load bearing capacity and extended lifetime expectancy. It has been indicated that slow release of the nanoparticles from the porous matrix onto the matting surfaces and the high lubricity power of such nanoparticles are responsible for the improved tribological behavior of such nanocomposites. Applications of such nanocomposites will be briefly discussed.

Further applications of nanocomposites containing the *IF* nanoparticles will be described.

## MINI-REVIEWS

### MR-1-119: Kinetics and Thermodynamics of SHS Reactions

**Jan A. Puszynski**

*Chemistry and Chemical Engineering Department*

*South Dakota School of Mines and Technology*

*501 E. St. Joseph Street, Rapid City, SD 57701, USA*

*Tel: 605/394-1230 Fax: 605/394-1232*

*E-mail: Jan.Puszynski@sdsmt.edu*

Self-propagating high-temperature synthesis has been explored and used for many years to produce various single phases and complex ceramic and intermetallic materials. During the past thirty years, a significant progress in the field of reaction kinetics and thermodynamics of condensed phase reactions has been made. This paper will present the key accomplishments and contributions in the area of gasless and gas-solid self-sustaining reactions. A special emphasis will be on thermodynamic, kinetics and microstructural aspects of the SHS processes.

### MR-3-176: Mechanical Alloying in the SHS Research

**F. Bernard<sup>1</sup>, E. Gaffet<sup>2</sup>**

<sup>1</sup>*LRRS, UMR5613 CNRS-Université de Bourgogne*

*BP 47870 - 21078 Dijon, France*

<sup>2</sup>*Far from Equilibrium Transitions Phases Group*

*CNRS UMR 5060 - 90010 Belfort, France*

The alternative processes which combine simultaneously or successively a ball milling and an SHS reaction are recent. However, these two synthesis routes have known an important improvement in the same period.

The Mechanical Alloying (MA) which is a powder processing technique allows the production of homogeneous materials starting was developed by J.Benjamin et al. [1] in 1960's. High energy ball milling and mechanical alloying of powder mixtures were reported to be efficient techniques for the preparation of nanocrystalline metals and alloys. Indeed, as mechanical processing technique, ball milling is effective for the production of micrometer size particles made of nanosize grains [2-5]. The mechanical alloying, a basically dry and a high energy milling process, is appropriate for the synthesis of all kinds of materials from metallic to ionic compounds [6,7].

Concurrently, in 1967 A.G.Merzhanov et al. [7] have discovered the solid flame phenomenon (i.e. the combustion process, in which starting reactants, the combustion products are in the solid state). From this period, this technique has received a wide attention [8-12] and is so - called SHS or combustion synthesis. The exothermic reaction between the reactant powders is initiated by an external heat source and becomes self-sustaining to yield the final product without requiring any additional energy. The SHS process saves time and energy since this processing technique proceeds in seconds or minutes compared to hours or days required in conventional and powder metallurgy routes [10,13,14].

Paradoxically, it was to await the beginning of years 1990 to observe a strong increase of the number of papers related to the combination of these two previously described techniques (MA and SHS). They can be classified as follows:

(i) the Mechanically-induced Self-propagating Reaction (MSR – 15,16) for which an SHS reaction occurs during milling inside the ball mill after some activation time, when the powder reaches a well defined critical state. A qualitative account of the ignition of combustion can be given as follows : when a mixture of the reactant particles is milled, the kinetic energy of the balls is used to heat the powder between the colliding balls. The temperature increase is about 50K to 300K. The reaction may start at the interface between two reactant particles within the compressed powder mixture. As a result, further local heating takes place. If the temperature at a nearby interface exceeds a critical value, the reaction is also initiated at that interface. Additional heat is released

and the reaction becomes self-sustaining. A combustion front develops and propagates through the powder. Most of the reactants are consumed within a fraction of a second, resulting in a macroscopically observable fast temperature increase.

(ii) the Mechanically Activated Self-Propagating High-temperature Synthesis (MASHS – 17-24) consists of a short duration high-energy ball milling step followed by a SHS. The first step is a mechanical activation where pure elemental powders are mixed in the appropriate stoichiometric ratio and co-milled in a planetary mill for a short time at a given set of milling parameters. The milling duration was chosen to be short to avoid the formation of mechanically-induced product phases, but still sufficiently long to form nanocrystallites. During the ball milling process, particles are repeatedly flattened, fractured, and welded. Fracture and welding are the two basic events which produce a permanent exchange of matter between particles and ensure mixing of the various elements of the powders. A balance between coalescence and fragmentation is achieved during the ball milling which leads to a rather stable average particle size. Finally, the mechanically activated mixtures were found to be composed of particles containing a nanodistribution of the elemental component. The effects of the milling conditions on the grain sizes and on the residual stresses were reported to modify the phase transformation kinetics in the final self-sustaining synthesis.

In this work, several examples extracted in both cases (i.e. MSR and MASHS) will be discussed in order to show, on the one hand, the influence of the ball milling conditions for inducing an SHS reaction inside the ball mill and, on the other hand, the role of the mechanical activation step on the SHS parameters and on the nature of end-products.

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## MR-2: SHS in Electric and Magnetic Fields

**Yu.M. Maksimov**

*The Department for Structural Macrokinetics of Tomsk Scientific Center of the Siberian Branch of the Russian Academy of Sciences, Tomsk, 634021 Russia*

The conduction of dc and low-frequency alternating electric field (EF) through powder mixtures intensifies the reactions proceeding in thermal explosion (A.G.Merzhanov, et. al.) and in layer-to-layer combustion (Z.A.Munir et.al.). The emission of Joule energy in the combustion front has, as a authors think, the dominating influence of reaction acceleration. Later, the non thermal influence of constant electric field on SHS was revealed (A.G. Merzhanov, *et.al.*). The combustion wave generates the ions, which acquire additional energy, forming new active centers, that leads to the change in combustion parameters. Owing to the complexity of the process, theoretic investigations of electric field action on SHS are limited only by dissipation, electric energy of the field (N.I.Kidin, I.A.Filimonov, A.Feng, Z.A. Munir) and the change in diffusion mobility of the substance in condensed phase (I.M. Kotin). These works don't consider the interaction of external and inherent electric field and macroscopic transfer of the substance in the wave.

The study of the effect of electromagnet field (EMF) on SHS restricted by consideration of electric energy only (V.I. Yukhvid, N.I. Kidin, K.G. Shkadinsky, S.Ye. Zakiev, *et.al.*). The possibility of EMF effect on the process kinetics wasn't studied.

The effect of constant magnet field on SHS is mainly limited to structural changes of the media in the combustion front (A.I. Kirdyashkin, Yu.M. Maksimov).

Recently electric motive forces were revealed in SHS (A.G. Merzhanov, Yu.G. Morozov, M.V. Kuznetsov) as well as a number of electrophysical phenomena including acoustic noise, EMF in high-frequency range (Yu.M. Maksimov, A.I. Kirdyashkin, V.S. Korogodov), super equilibrium emission of carriers of electric charge from condensed substance (B.A. Kudryashov, A.S. Mukasyan, A.I. Kirdyashkin, V.S. Korogodov, *et.al.*). Works of these authors show, that the mechanism of electrophysical phenomena of the combustion wave is complex one and needs further investigation.

## MR-4: SHS-Produced Composite Materials

**Sheng Yin**

*Department of Powder Metallurgy  
University of Science and Technology Beijing  
Beijing 100083, China*

The research, development and application of the composites have been carried out widely and deeply in recent years. Among the methods for producing the composites, such as powder metallurgy, CVD, PVD, infiltration, slurry casting, ospray, XD etc., SHS is one of favorable and important technique. This paper reviews the SHS-produced composites composed of ceramic matrix composites, metal matrix composites and intermetallic matrix composites.

As for the ceramic matrix composites, SHS is effective one of the techniques for obtaining the fine particle and uniform distribution. Combined with the densifying methods, SHS can be used to produce bulky materials with the uniform microstructure. The samples of the ceramic matrix composites are composed of TiC matrix composites, TiB<sub>2</sub> matrix composites and Al<sub>2</sub>O<sub>3</sub> matrix composites.

The metal matrix composites is composed of aluminum and titanium matrix composites. The intermetallic matrix composites is composed of NiAl and TiAl matrix composites. Their producing methods and properties are detailed discussed.

**Key words:** SHS, composites, ceramics

## KEYNOTE LECTURES

### K-9-13: Critical Phenomena at Autowave Propagation

**E.N. Rumanov**

*ISMAN, RAS, Chernogolovka, 142432 Russia*

Speaking on autowave critical phenomena we mean qualitative changes in the wave behavior, jumps in its velocity and magnitude, and sometimes quenching. From mathematical viewpoint, the confluence of stable and unstable branches of the wave problem solution takes place, or the unstable branch between two stable ones vanishes. There is a good number of examples of such behavior. It is manifested by combustion waves as well as other autowave processes (optical discharge, evaporation of superheated liquid, recombination of freeze radicals, etc.).

The jumps and hysteresis in question are due to changes in the wave propagation individual mechanism. At the same time, the waves at critical conditions have some general property, chaotic pulsating at a narrow interval of parameters near the bifurcation point. This pulsating is large as compare to the thermal critical fluctuations of continuous phase transitions. Their scale is similar to that of turbulence. However, they differ strongly from the ordinary turbulence. We deal with a new sort of chaos.

The review report talks about the autowave critical phenomena in comparison with those of phase transitions. The examples of the wave transformations are discussed. We focus on a feedback acting in each case. Theoretical results and computational data concerning to the chaotic behavior near the bifurcation point will be also presented.

### K-5-179: Dynamics of Hot Spots in Solid Flame Propagation

**B.J. Matkowsky**

*Department of Engineering Sciences and Applied Mathematics*

*Northwestern University*

*Evanston, IL 60208 USA*

We consider modes of gasless solid fuel combustion waves, which are employed in the SHS (Self-Propagating High-Temperature Synthesis) process for the synthesis of advanced materials. In this process a finely ground powder mixture of desired reactants is ignited at one end. A high temperature thermal wave then propagates through the sample converting reactants to products. The SHS process was pioneered in the former Soviet Union and offers the promise of significant advantages in materials synthesis over conventional processes.

Consider the burning of a cylindrical sample of solid fuel. The sample is ignited at one end and synthesis proceeds as a high temperature combustion wave propagates along the cylinder. In the simplest case the combustion wave has a uniformly propagating planar front separating the burned from the unburned sample, the temperature distribution along the front is uniform and the speed of the wave is constant.

However, it is known both theoretically and experimentally that nonuniform modes of propagation are possible. Generally, these modes arise via bifurcations as parameters of the problem are varied. The study of different modes of propagation is significant since the nature of the combustion wave determines the conditions for synthesis, which affect the microstructure of the material produced. Indeed, some materials can only be synthesized in a nonuniform mode.

We describe a variety of nonuniformly propagating modes. These include planar pulsating combustion, sometimes referred to as autooscillatory combustion, in which planar fronts with a uniform temperature dependence on the front propagate with oscillatory velocities. They arise when the radius of the cylinder is sufficiently small. Nonplanar modes of propagation typically occur when the radius of the cylinder is sufficiently large. These modes are generally characterized by dynamics involving one or more hot spots (localized high temperature maxima) along the

combustion front.

These modes include (i) spin combustion, in which one or more hot spots move in a helical fashion along the surface of the cylinder, all in the same direction, as the combustion wave propagates, (ii) counterpropagating combustion in which spots travel in opposite directions and undergo complex interactions when they collide, e.g., apparent annihilation and creation, or passage through each other, unchanged except for a phase change (as is the case with solitons), and (iii) multiple point combustion, in which hot spot(s) repeatedly appear, disappear and reappear.

The above modes are described as symmetric traveling waves, i.e., in the case of multiple hot spots, all spots are identical and are equally spaced around the circle as they propagate. We also describe new types of spin combustion, including (iv) asymmetric traveling waves, in which two nonidentical spots, not equally spaced around the circle, spin together as a traveling wave, or as a modulated traveling wave. The leading spot has a higher temperature than the trailing spot. Nevertheless, the two spots are bound together as they travel, separated by angle  $\alpha$ . Thus, the term bound states has been used to describe this mode. Finally, we describe (v) spontaneous creation of spots followed by counterpropagation and annihilation.

## **K-11-180: Electrothermal Explosion (ETE) Method to Study the Kinetics of Fast High-Temperature Reactions in Condensed Systems**

**A.S. Shtenberg**

*Semenov Institute of Chemical Physics of RAS, Moscow, Russia*

*Micro Assembly Technologies, Richmond, USA*

ETE is an adiabatic thermal explosion in a system, which has been heated up to a given temperature  $T_0$  in a fast (several seconds), spatially homogeneous mode. Presently we have results of ETE studies for a great number of condensed electroconductive systems. Direct flow of current or the effect of high-frequency field is used for heating. The cylinder samples are pressed from a mixture of powder reagents (Ti+C, Ta+C, Si+C, Ti+B, B+C, Si+Ti, W+B, Ti+Fe<sub>2</sub>O<sub>3</sub>, Mg+B, etc.) or assembled from a large number of alternating thin foils made from reagents (Ni+Al, Ti+Al, Ni+Ti, Ti+C (condensed products of pyrolysis of a thin paper ribbon, etc.). The lecture presents the current state of ETE theory, including the specificities of the process, which are based on differences in the mechanism of interaction (reaction diffusion, reaction dissolution) among the components of SHS-mixture. Data on state-of-the-art ETE equipment are presented (operating temperature range from 1000 to 4000 K, times of total conversions less than  $10^{-4}$  s). The central part of the lecture is devoted to the radically new experimental macrokinetic and kinetic results of studying heterogeneous condensed systems.

Solid-phase reactions. Reaction diffusion dominates in the heating of the majority of gasless SHS systems up to the melting point of the malleable component. The example of Ta+C powder mixture demonstrates the important role played by thermally-activated sintering of the powders of initial components in the acceleration of such process. Reactions with a liquid phase. The example of ETE in systems Ti+C, Si+C, Al+Ni, Al+Ti, etc. demonstrates the leading role played by dissolution in the interaction of reagents at temperatures above the melting point of the malleable component (here Ti, Si, Al, etc.). The same coefficient of liquid-phase diffusion  $D_L = 10^{-5}$  cm<sup>2</sup>/s for all liquids (Ya. I. Frenkel) explains the approximate similarity of heat-release macrokinetics for all SHS systems (studied by ETE method up to now) of gasless combustion with the prior melting of one of the components in SHS front. The author believes that this macrokinetic mechanism is responsible for the similarity of gasless combustion rates in many binary SHS mixtures, even though their constants of solid-phase reaction diffusion differ by several magnitudes. Data from the theory of combustion rate of the above listed systems, based on the mechanism of "reaction dissolution", is presented. Specifically, it is demonstrated that the theory, developed with the author's participation, is in great quantitative agreement with experiments of other researchers in a wide range of SHS rates—from 0.5 cm/s to 15 m/s. In the concluding part, new data on kinetics of high-temperature conversion in termites, for ETE with microwave heating, is analyzed. Additionally, possibilities of

a new methodology for electrothermal analysis (ETA), which is the development of ETE, are considered. In contrast to traditional ETE, ETA can be used to study the kinetics of fast endothermal reactions such as polymer pyrolysis.

### **K-10-59: Mutual Interdependence between SHS Reaction and Gas Infiltration during Thermal Explosion**

**K.G. Shkadinskii**

*Chernogolovka, Institute of Problems of Chemical Physics, Russia*

The results of the theoretical investigation of the exothermic chemical interaction between the porous medium and the active gas reagent in report are presented. We consider case when the interaction products are solid and form new porous matrix. These investigations are important for the nitrides, hydrides and oxides synthesis. On the other hand the mathematical models for these compositions are simple relatively other complicated the porous-gas systems, where gas can be multicomponent and solid is multicomponent mixture.

The investigations direct to analysis of the thermal explosion conditions. In frames of the simplified model we give the analytical conditions of the thermal explosion, which extend Semenov's theory on the porous-gas interaction. It is analyzed where Semenov's theory works and where new criterions are necessary. The exothermic chemical interaction can be controlled by the gas filtration. More complicated models were studied by the numerical methods.

The investigations are aimed at determination of the macrokinetic laws of the porous-gas interaction. We defined and described the layered and frontal stages of interaction by the analytical and numerical methods. Dynamics of this interaction is the foundation of the macrokinetic laws, which depend on the filtration transport and the heterogeneous kinetics.

The results of investigations of the postinduction periods of the thermal explosion are interesting when the thermal explosion is used like the technological method of SHS. There was studied dynamics of the chemical interaction depending on the gas pressure, the thermokinetic parameters and the filtration conditions. The nonstationary frontal regimes, which arise here, were analyzed. Information about the temperature distribution and the propagation velocity can be used at production of the functional gradient materials.

### **K-13-38: On Spinning Modes of Gasless Combustion**

**L. Kagan<sup>1</sup>, G. Sivashinsky<sup>2</sup>**

<sup>1</sup> *School of Mathematical Sciences, Tel Aviv University*

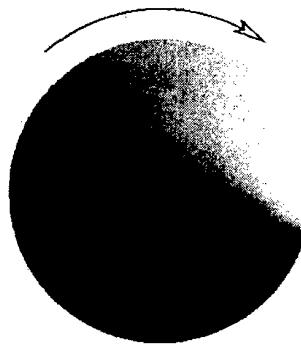
*Ramat Aviv, Tel Aviv 69978, Israel*

<sup>2</sup> *The Benjamin Levich Institute for Physico-Chemical Hydrodynamics*

*The City College of New York, New York, NY 10031, USA*

A conventional three-dimensional model for gasless combustion of a cylindrical sample is studied numerically. In line with the earlier theoretical findings several distinct modes of combustion waves are identified. At sufficiently high activation energies the steady planar wave becomes unstable assuming a galloping or spinning structure (depending on the system's parameter range). In contrast to previous analytical results based on the reactive interface approximation, it is found that the spinning mode may emerge not only as a subcritical (inverted) bifurcation of a steady planar wave, but also as a normal supercritical bifurcation.

The transition from the galloping to spinning modes and formation of more complex spatio-temporal structures in wide cylinders is discussed as well.



**Figure.** Distribution of maximum temperature in the regime of spinning propagation.  
Lighter shade corresponds to a higher temperature.

### K-3-195: The Present Status and Trends of SHS FGM

**Chang-Chun Ge**

*Laboratory of Special Ceramics and Powder Metallurgy*

*University of Science and Technology Beijing, Beijing 100083, China*

SHS is an advanced technology for fabricating FGM. Apart from well-known features of SHS, the following advantages in making FGM with SHS technology is remarkable:

- (1) High reaction rate and short duration at high temperature are very beneficial for keeping the designed constitute gradient in FGM;
- (2) Simultaneous synthesis and densification can be realized;
- (3) Products with large dimensions or compositional shapes can be made.

This lecturer reviews the present status of SHS FGM and shows the trends of SHS FGM.

According to the formation mode of graded structure, SHS FGM can be fabricated with three different kinds of green compacts --- from a graded powder stack; from a two-layered powder stack by controlled infiltration during reactive processing, or from a compositionally homogeneous powder stack by controlled phase separation in multi-component melt produced during SHS or by heat-treatment after SHS and densification.

According to the densification mode of graded structure, SHS FGM can be fabricated with various consolidation processes --- uniaxial hot-pressing, gas pressure sintering or hot-isostatic pressing (HIP), pseudo-HIP, consolidation with centrifugal force, explosive forming etc.

Various FGMs fabricated by SHS with different formation modes of graded structure and consolidation processes are listed and typical examples with their features are illustrated.

Despite many progresses have been made on SHS FGM in research laboratories, there are few success on production and commercialization of SHS FGM. The authors analyze the cause of this situation and suggest the future R&D direction of SHS FGM.

### K-2-189: Reactive Castings of Ceramic Composites

**Nils Claussen**

*Advanced Ceramics Group, Technische Universität Hamburg-Harburg, Germany*

Reactive casting of ceramic composites may become a low-cost, fast, and simple manufacturing route to high-performance components. In many cases, near-net shapes are obtainable. Al-alumina composites made by (directed molten metal oxidation) or (reactive melt penetration) exhibit improved fracture toughness and thermal shock resistance, which, however, can be more readily be achieved by just infiltrating Al into porous alumina preforms. For a number of applications though, Al-containing composites do not meet the required properties such as refractoriness, stiffness, or wear and erosion resistance. Therefore, other metal-ceramic systems have been studied which exhibit high fracture toughness even to temperatures as high as 800°C. However, direct liquid infiltration of such refractory metals into precursors is complicated and expensive, partially because

of the high infiltration temperatures and the costs of the prealloyed metals. An acceptable solution seem to be reaction processing techniques.

In this lecture, reactive infiltration techniques presently being developed in the Advanced Ceramics Group of TUHH, are discussed with respect to their special features and advantages. These methods make use of low-temperature ( $< 700^{\circ}\text{C}$ ) processing, which then result in composites having melting points  $> 1000^{\circ}\text{C}$ , e.g. i-3A (reactively infiltrated  $\text{Al}_2\text{O}_3$ -aluminide alloys); isi-3A (in situ-infiltrated 3A); i-MMC (reactively infiltrated metal-matrix composites); isi-MMC (in situ-infiltrated MMC).

### **K-8: SHS of Complex Ceramic Materials and Their Properties**

*Roman Pampuch, Jerzy Lis*

*Department of Advanced Ceramics, AGH*

*Cracow, Poland*

It is well known that properties of ceramic materials depend strongly on the method of their production this being due to homogeneity of the material varying with the method. Improvement of the homogeneity has been achieved by using, among others, the sol-gel method, organic precursors and mechanical alloying. It shall be demonstrated in the paper that the SHS method permits to obtain a homogeneity of the materials which is comparable to the high one achieved by using more complex and less energy efficient methods. This is illustrated on hand of examples including materials based on complex ternary compounds and compounds of the T2-B2 type,  $\text{SiC-Si}_3\text{N}_4$  nanocomposites,  $\text{SiC-TiB}_2$  composites and solid solutions in refractory ceramic systems.

### **K-12-198: SHS $\text{TiB}_2$ Based Multiphase Ceramics and Composites**

*R.Z. Yuan, Z.Y. Fu, H.Wang, W.M. Wang, Q.J. Zhang*

*State Key Lab of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, P. R. China*

$\text{TiB}_2$  ceramics have distinguished characters, such as high hardness, high melting point, high elastic modulus and good electric conductivity.  $\text{TiB}_2$  based multiphase ceramics and composites can maintain some of these characters, or can be adjusted to an expected property by using of these characters and suitable techniques. In this paper, following materials were fabricated and analyzed: ceramics and multiphase ceramics, as  $\text{TiB}_2$ ,  $\text{TiB}_2\text{-TiC}$  and  $\text{TiB}_2\text{-Al}_2\text{O}_3$ ; cermets, as  $\text{TiB}_2\text{-Fe}$  and layered composites, as  $\text{TiB}_2\text{-metal}$ . Two ways based on SHS process were used in fabrication of these materials. One way is synthesizing powders by SHS and then gets densified materials by sintering, the other one is combining synthesis and densification in one step by a so-called SHS/QP technique.

## ORAL PRESENTATIONS

### **O-3-88: The Application of Mechanical Activation to the Performance of Solid-State Combustion Regime in SHS-Systems**

*M.A. Korchagin, T.F. Grigorieva, B.B. Bokhonov, A.P. Barinova, N.Z. Lyakhov*

*Institute of Solid State Chemistry and Mechanochemistry*

*Novosibirsk, Russia*

Using preliminary mechanical activation (MA) of the SHS-systems in high-energy planetary ball mill of the AGO-2 type, we successfully realized the solid-phase combustion regime in some compositions of the systems Ni-Ti, Ni-Si, Fe-Si and Ni-Al. In the present report we describe the results of longer investigation of the discovered effect of preliminary MA on the transition from the interaction between reagents with the participation of liquid phase to real solid-phase interaction in the combustion wave. The compositions selected for the experiments did not provide SHS without additional heating of usual powder mixtures (Ni+45 mass.% Ti and Ni+13 mass.%Al). The dependencies of burning velocity ( $U_c$ ) and temperature ( $T_c$ ) on the time of MA were determined experimentally for these compositions using three steps of mill operation differing by energy output. For all the investigated MA regimes, these dependencies are curves with maximums. It was stated as a result of the investigations that the very possibility of SHS to occur in these compositions without heating, and further increase of  $U_c$  are connected with the processes involving the transformation of powdered mixtures into «layered composites» in which the reagents are substantially dispersed, their contact area increases and high concentration of defects is created. It was stated in electron microscopic studies that as early as after MA for 1-2 min, the reagents grain size in composites does not exceed 50 nm, while minimal size is 10-20 nm. An increase of MA time leads to the formation of the structure with higher defect content, in which the grains are observed in Moir patterns. A decrease of  $U_c$  after maximum is due to the poisoning of the reaction mixture with the products of mechanical alloying. It was discovered that the poisoning can be understood not only as the beginning of the formation of intermetallic compounds during MA (which is really observed with some MA regimes), but also heat poisoning. As the time of mechanical activation increases, temperature in vials increases; this causes the annealing of the induced defects and even the increase of grain size. For all the compositions and regimes of mechanical activation, the conditions and duration of preliminary MA, required for the solid-phase interaction to be realized in SHS regime, were determined. The products of solid-phase combustion are absolutely indistinguishable by their morphology from the initial samples and have ultrafine grain size. By means of DTA and DSC investigations we revealed a substantial decrease of temperature at which heat evolution starts in the mechanically activated samples in comparison with non-activated powdered mixtures. Heat evolution occurs at lower temperatures and in several stages that are elongated over temperature scale. This sequence of stages is connected with the stage sequence of defect annealing, as well as with the stage sequence of the solid-phase interactions of reagents. This is the main reason why solid-phase SHS regime can be carried out even in the composition including such an easily melting reagent like aluminum. It is completely consumed in the leading region of the combustion wave at a temperature much below the melting point of the most easily melting eutectics in the Ni-Al system. This phenomenon is also the reason of anomalously low  $T_c$  of mechanically activated samples. Since the evolution of heat in the samples after MA occurs at lower temperatures and in several stages elongated over temperature scale, this leads to the decrease of heat evolution rate and thus to the decrease of  $T_c$ . In mechanically activated samples, solid-phase combustion is realized according to the relay race mechanism; this leads to a complicated dependence of  $U_c$  on  $T_c$ .  $T_c$  is determined by heat evolution processes in the interactions of ultrafine reagents inside the layered composites, while  $U_c$  depends on temperature conductivity from the hot composite to cool one. The results obtained in experiments involving the combustion of mechanically activated samples at increased initial temperatures are the evidence that non-equilibrium defects created as a result of MA do not have

enough time to get annealed in the heating region and are conserved in the sample till the beginning of the chemical interaction itself in the leading region of the SHS wave. This leads to a very unusual phenomenon, i.e. the combustion can be carried out during the solid-phase interactions in mechanically activated samples while heat explosion cannot. The *in situ* experiments on the heating of mechanically activated samples in electron microscope column have been carried out.

#### **O-4-29: Catalytic Gas Nitriding of Metals and Alloys – 5 Years of Scientific Development and Practical Application**

*Vladimir Ya. Syropyatov, Viktor V. Barelko, Valentin M. Zinchenko, Leonid A. Bykov*

*NIITAvtoprom Moscow, Institute of Problems of Chemical Physics, RAS*

*and JSC "Chemphys" Chernogolovka*

The report is reviewed results of scientific development and industrial implementation of the new method of metal surfaces' nitriding on the base of catalytic treatment of furnace atmosphere for last five years after its creating. Ideology of the method uses the notions about non-equilibrium high-active state of gas reacting medium after short-time of its contact with catalyst. The authors have shown theoretically and proved in actual practice the possibilities of the essential widening of the nitriding process possibilities and the receiving of unique parameters in treating metal articles by introduction into the traditional muffle nitriding furnace a catalytic element being able to regulate the transformations of the nitriding ammonia-air furnace atmosphere at the "in situ" regime.

Laboratory experiments and real practice verified the correctness of the common idea and initial premises. The new nitriding process have changed its character very strongly both in the regime parameters and the qualities of the article treated:

- the alpha-solid solution range was very widened;
- the control of the final nitrogen content in steel articles was realized in the range which is inaccessible under the traditional non-catalytic nitriding;
- the corrosion resistance of structural steel was increased;
- the hardness of the treated article was increased to the depth more than 1 mm;
- the decarbonizing process during the nitriding was strongly depressed;
- the nitriding process was sufficiently accelerated simultaneously with the multiple decrease of the ammonia consumption.

The new ideological approach allowed to discover new possibilities of nitriding operations which can not be realized in the traditional nitriding regimes:

- special anti-corrosion nitriding;
- high-speed cutting steel nitriding;
- nitralloys nitriding;
- forming-tools nitriding;
- stainless steels nitriding;
- powder metallurgy articles nitriding;
- Ti-alloys nitriding.

Up to now the process of catalytic nitriding has been realized and successfully used on industrial scale at seven Russian plants.

#### **O-2-114: Ceramic Lined Steel Elbow Made by SHS-Gravitational Process**

*Tao Lin, Sheng Yin, Zhimeng Guo, Shiju Guo*

*Department of Powder Metallurgy, University of Science and*

*Technology Beijing, Beijing 100083, China*

The ceramic lined steel pipe made by SHS-centrifugal process has the advantages of wear resistance, corrosion resistance, thermal-shock resistance and mechanical shock resistance, and has

been widely used to transport coal, coke, coal cinder, mineral powder, cement mortar, molten aluminum and oil-water.

However, the SHS-centrifugal process only can be used to synthesize the linear pipe with the diameter being larger than about 20 mm due to some limitations of the principle. The fine pipe and the elbow can not be produced by SHS-centrifugal process. These obstacles can be surpassed by SHS-gravitational process, i.e., with the aid of the gravity to achieve the separation of molten ceramics and metal and subsequently the ceramics solidifying to form the ceramic lined layer.

In this paper, the effects of filling density, aluminum powder size, preheating temperature and additives on the ceramic lined steel pipe made by SHS-gravitational process were studied. It shows that the propagating rate of the combustion wave along the steel pipe decreases with increasing the filling density, and increases with increasing the preheating temperature. The combustion rate of the thermite with fine aluminum powder is faster than that of the thermite with coarse aluminum. Furthermore, it becomes controllable with the addition of suitable additives such as  $\text{SiO}_2$  and  $\text{CrO}_3$ . The density of the ceramic layer is  $3.53 \text{ g/cm}^3$  and the hardness(Hv) is 1235. The microstructure of the ceramic layer is composed of corundum and spinel.

Coal powder nozzle with the diameter of 20 mm produced by SHS-gravitational process has been used in blast furnace. The elbows with the diameter of 20-325 mm were also produced by this process. The tapered pipe has also used in the mineral-dressing.

**Key words:** SHS; termite; gravitation; ceramics

#### **O-1-60: Chemical Activation of SHS of Aluminum and Titanium Nitrides**

*Valery Rosenband, Alon Gany*

*Faculty of Aerospace Engineering, Technion – Israel Institute of Technology, Haifa  
32000, Israel*

The difficulties of aluminum and titanium particles nitridation results from protective layers of  $\text{AlN}$  and  $\text{TiN}$  respectively, which form on the particles surfaces, so that nitridation of the metal is determined by the diffusion of nitrogen atoms through this protective layer. To accelerate the aluminum and titanium nitridation process we suggest in this work to add to the initial metal powder some amount of ammonium chloride  $\text{NH}_4\text{Cl}$ . During thermal decomposition of  $\text{NH}_4\text{Cl}$ , molecules of hydrogen chloride  $\text{HCl}$  are formed, which can react with the metal to form gaseous chlorides. These chlorides being formed on the nitride/metal interface, can break the surface nitride layer due to appearance of tensile stresses. In such a case, the layer becomes non-protective and does not prevent the access of nitrogen to the metal surface. This work investigated the influence of the amount of  $\text{NH}_4\text{Cl}$  in mixture with the metal, metal particle size, porosity of the pressed sample, and nitrogen pressure on the extent of metal conversion into nitride. Experiments were carried out in both combustion and thermal explosion modes of SHS. The extent of aluminum and titanium nitridation was estimated through the weight growth, as well as by X-Ray diffraction, EDX and chemical analysis. It was shown that the addition of  $\text{NH}_4\text{Cl}$  promotes the rate of aluminum and titanium nitrides formation. Almost full extent of metal conversion into nitride can be achieved already at low content of  $\text{NH}_4\text{Cl}$  of about 5 wt%. Of particular interest is that with  $\text{NH}_4\text{Cl}$  the process of aluminum and titanium nitriding in the combustion mode takes place already at nitrogen pressures as low as 5-10 atm.

#### **O-2-200: Chemical and Structural Transformations in Shock-Loaded Titanium- Carbon Powder Mixture**

*Yu.A. Gordopolov, S.S. Batsanov, S.I. Gavrilkin, A.Yu. Gordopolov*

*Institute of Structural Macrokinetics and Materials Science*

*Russian Academy of Sciences*

*Chernogolovka, Moscow Region 142432, Russia*

It is known, a wave of combustion can be readily initiated in the  $\text{Ti}-\text{C}$  system upon local heating (in a point or plane). In this case, propagation of the reaction zone is sustained by heat conduction.

The wave leaves behind a combustion product, TiC. This reaction represents a classical example of SHS. In this system, TiC is also known to form under the action of a shock wave, but the reaction mechanism has been studied inadequately. In particular, it remains unclear whether the pressure jump only initiates chemical reaction (that is then completed in the combustion mode) or reaction proceeds within the shock wave (shock-wave synthesis). This dilemma is the focus of our work.

In our experiments, we used the powders of Ti and C with a particle size of 20 and 5  $\mu\text{m}$ , respectively. A 50 : 50 green mixture (initial porosity 30%) was placed in a special recovery fixture. A shock wave in a sample was induced by explosive loading systems utilizes both plane and cylindrical wave generators. The geometry and design of experimental setup ensured propagation of planar or conical shock waves in a sample and excluded the interfering action of reflected or rarefaction waves. The dynamic pressure  $P$  applied to samples could be varied between 38 and 240 kbar. The conversion degree was estimated by x-ray diffraction and structure analysis. For  $P < 56$  kbar, chemical reaction was found to proceed in the combustion mode (as a post effect). For  $P$  around 56 kbar, no reaction was detected altogether ("dead" zone). For  $P > 145$  kbar, chemical reaction was found to proceed (at least partially) within the shock wave, that is, in the mode of shock-wave synthesis. The last fact was proved by Hugoniot and Mach's disk diameter measurements. Therefore, the mechanism of shock-induced reaction was found to be strongly dependent on shock wave parameters.

#### **O-3-104: Combustion Modes for Highly Diluted Ti+2B System**

*S. G. Vadchenko, I.A. Filimonov*

*Institute of Structural Macrokinetics and Materials Science*

*RAS, Chernogolovka, 142432 Russia*

In this work, combustion modes for Ti+2B system with high concentrations of copper and iron additives (65-83 % wt) have been investigated in argon atmosphere under air pressure. Additives concentrations, initial temperature of samples and particle size of initial components varied.

Experimental technique based on using long samples (length/diameter ratio  $\sim 5-12$ ) produced with compacting green mixture on alumina capillaries. Inside the capillary, there was a heater of molybdenum wire which heated the sample to the desired temperature, up to the thermal explosion one. Combustion was initiated with a filament that was located at the end surface of the sample. Combustion process was filmed with a video-recorder, then combustion rate was determined with frame scan of videotape recording. Selected products were studied by X-ray analysis, and their microstructure was investigated by SEM.

The results of the research showed three temperature modes of combustion (spin, high-rate and low rate) in the given systems. Their parametric domains of existence were defined. The peculiarity of the systems combustion is the low-rate stationary combustion mode that was found earlier only in metal-gas systems. The value of combustion rate in the low-rate mode can be of lower order than that in the high-rate mode, and the temperature can be more than 300°C lower. Spin modes occur in the conversion region of low- into high-rate combustion mode.

Examination of the obtained results show that some structural factors associated with either agglomeration, or inert additive melting, or intermediate products can influence greatly on realization of different modes.

#### **O-4-55: Continuous SHS Technology and Properties of Soft Magnetic Ferrites**

*P.B. Avakyan<sup>1,2</sup>, M.D. Nersesyan<sup>2</sup>, A.G. Merzhanov<sup>2</sup>, J.T. Richardson<sup>3</sup>*

*<sup>1</sup>Scientific and Industrial Center SHS, Yerevan, 375010 Armenia*

*<sup>2</sup>Institute of Structural Macrokinetics and Materials Science, RAS Chernogolovka, 142432 Russia*

*<sup>3</sup>Department of Chemical Engineering, University of Houston, Houston, TX 77204, USA*

SHS-based continuous technology of magnetic soft Mg(Mn,Ni)-Zn ferrite materials was developed for industrial application. Experimental diagnostics of combustion mechanisms and structure

formation in SHS-processes were conducted to generate necessarily data for developing a continuous technology. The optimal synthesis conditions (solid reactant composition, reactant particle size, gas environment and its flow rate) and the synthesis-properties relationship were determined during experiments.

Taking into account that the properties (quality, particles size and distribution) of initial components have an impact on the sintered ferrite articles, the optimal conditions of treatment of the combustion product into high quality articles were developed. These investigations included determination of grinding regimes, forming, amount of binder, and sintering conditions (its temperature regimes and duration).

Several design and operation of a continuous laboratory process will be discussed. This part of study includes determination the stability of the temperature front motion in the reactor, development the best way to feed the green mixture (powder, granules, briquettes), ignition procedure, impact of gas environment, thermal regimes of the process on the produced product properties, etc.

Supported in part by the US Civilian Research and Development Foundation (CRDF) Grant AC2-2211.

#### **O-2-78: Densification of High-Melting Point Nitrides Compounds under Self-Propagating High-Temperature Synthesis**

*K.L. Smirnov, I.P. Borovinskaya*

*Institute of Structural Macrokinetics and Materials Science*

*Russian Academy of Sciences, Chernogolovka, Russia*

The main two factors that determine density of nitride ceramics synthesised by self-propagating high-temperature synthesis in "gas-solid" reactive systems was found experimentally:

- volume change during nitriding, dominating in case of synthesis BN-based ceramics;
- sample shrinkage caused by pressure gradient of reaction gas (nitrogen) around combustion zone.

The last factor is most valuable for densification of such ceramics as TiN, TaN, AlN,  $\alpha$ - and  $\beta$ -SiAlONs.

The intensity of sample shrinkage simultaneously depends on nitrogen pressure in SHS reactor, starting sample diameter, content of combustible and low-melting component in green mixture. In some systems sample shrinkage is accompanied by plastic deformation of product. For example, the  $\beta$ -sialons grains decrease and obtain irregular shape with distorted boundaries, completely losing their traditional morphology of elongated hexahedral prisms. At same time the X-ray structure analysis data show disordering of their interlayer space along crystal c-axis.

In all considered reactive systems the most favourable conditions for synthesis of high-dense ceramics with uniform structure was realized under high-pressure nitrogen (100 MPa and more). Under such conditions the infiltration combustion fully transform to the layer-by-layer mode and the combustion parameters (burning velocity and combustion temperature) attain their maximum values ( $u_b=1.5\text{--}9$  mm/s and  $T_c=2300\text{--}2800^\circ\text{C}$ ). As the result we was successful in obtaining nitride-based ceramics with relative density 0.9 and higher.

This work is supported by Russian Foundation for Basic Research, grants RFBR 99-03-32258, 00-15-99054.

#### **O-2-79: Dynamics of Phase Formation During Combustion of the Ti-B and Ti-C Systems in Nitrogen and Air**

*D.Yu. Kovalev, V.M. Shkiro, V.I. Ponomarev*

*Institute of Structural Macrokinetics and Materials Science*

*Russian Academy of Sciences, Chernogolovka*

*Moscow Region, 142432 Russia*

The researches of combustion of heterogeneous mixes titanium with boron and titanium with carbon are carried out at the presence of a not inert gas phase in conditions of self-propagation

high-temperature synthesis (SHS). The mechanism of interaction of components at infiltration of reacting gas in system solid-solid-gas with an opportunity of course of consecutive and parallel reactions is offered.

By a method of time-resolved X-ray diffraction analysis, for the first time directly in a wave of combustion, experimental data on a sequence of phase formation in the  $Ti-xB-N_2$  and  $Ti-xC-N_2$  systems are received. It is shown, that the reaction, without dependence from stoichiometric of mixes and pressure of a gas, begins with interaction between titanium and nitrogen. Temperature of initiation of process makes  $\sim 600^\circ C$ .

In system  $Ti-0.5B-N_2$ , in the combustion wave, solid-state reaction titanium with nitrogen originally proceeds with consecutive formation  $Ti_3N$  and  $TiN$ . The interaction titanium with boron occurs at later stages of process in a post-combustion zone. The composition of final product in volume is multiphase - titanium boride ( $Ti_3B_4$ ,  $TiB$ ,  $TiB_2$ ) and titanium nitrite ( $TiN$ ,  $Ti_3N$ ), which is a consequence of gas infiltration condition. On a surface a dominant phase is  $TiN$ .

In system  $Ti-B-N_2$ , the reaction is carried out by parallel interaction melting Ti with boron and nitrogen with formation of two phases -  $TiN$  and  $TiB_2$ . On a surface, after passage of a combustion wave, the gradual reduction, up to a level of a background, intensity of peak  $TiB_2$  is observed.  $TiN$ , generated in a surface layer, is characterized by the increased period of a lattice, that is connected to dissolution in him boron from  $TiB_2$ . In volume, alongside with titanium nitrite, the titanium boride  $TiB$  and  $Ti_3B_4$ , formed for front of combustion wave at interaction superfluous Ti with  $TiB_2$ , are present.

The researches of phase formation dynamics are carried out at combustion mixes  $Ti-xC$  with  $x = 0.5$  and  $1.0$  in nitrogen. It is shown, that in system  $Ti-0.5C-N_2$ , in the combustion wave front, the interaction begins with formation  $Ti_3N$  and  $TiC_{0.5}N_{0.5}$ . In the post-combustion zone the disappearance of  $Ti_3N$  peaks is observed and on a surface is formed titanium carbonitride with the greatest possible concentration of nitrogen -  $TiC_{0.5}N_{0.5}$ . Content of nitrogen in titanium carbonitride decreases on depth of a sample and in the central part there are only  $TiC_{0.5}$ .

In system  $Ti-C-N_2$ , the reaction transpire by simultaneous interaction melting Ti with carbon and nitrogen with formation of two phases -  $Ti_3N$  and  $TiC$ . Temperature in front of combustion exceeds melting temperature  $Ti_3N$  and its fast disappearance is observed. Titanium carbide does not cooperate with nitrogen and a final product of SHS reaction is stoichiometric  $TiC$ .

The results on dynamics of phase formation are given at combustion mixes  $Ti-xB$  and  $Ti-xC$  on air. It is shown, that the presence of oxygen, essentially does not change a sequence of course of reactions of synthesis in the considered heterogeneous systems. The oxidation of a surface layer of products of combustion ( $TiN$ ,  $TiC$  or  $TiC_{0.5}N_{0.5}$ ), with formation of rutil ( $TiO_2$ ) occurs at cooling samples up to temperature  $\sim 800^\circ C$ . Structures of final products in volume of samples are similar to structures received at realization of synthesis in nitrogen.

This work was supported by the Russian Foundation for Basic Research (grant 00-15-97370).

### **O-3-91: The Effect of Mechanical Activation on Self-Propagating High-Temperature**

#### **Synthesis of Barium Hexaferrite**

*T.L. Talaka<sup>1</sup>, A.V. Belyaev<sup>1</sup>, A. Ph. Ilyushchenko<sup>1</sup>, A. Letsko<sup>1</sup>, M.V. Kuznetsov<sup>2</sup>, Yu.G. Morozov<sup>2</sup>, Zhengyi Fu<sup>3</sup>, Runzhang Yuan<sup>3</sup>*

<sup>1</sup>*Powder Metallurgy Research Institute with Pilot Plant, Minsk, Belarus*

<sup>2</sup>*Institute of Structural Macrokinetics and Materials Science, RAS  
Chernogolovka, 142432, Russia*

<sup>3</sup>*State Key Lab of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, China*

Due to its large coercive force M-type hexagonal ferrite  $BaFe_{12}O_{19}$  in its pure and substituted forms is widely used in magnetic recording applications. Self-propagating high-temperature synthesis (SHS) shows promise as an effective alternative to the furnace ferritization step of ferrite production technology. However, during a self-sustained reaction material state can strongly

fluctuate, leading to variations in phase composition, morphology, crystal structure and physical properties of a product. Charge mixture composition and reactive gas pressure commonly used to control combustion conditions do not provide the accuracy required. This fact limits wide commercial use of the SHS for production of hard magnets with precision characteristics.

This work evaluates potential of mechanical activation (MA) as an additional factor to adjust combustion conditions as well as final material structure and properties of  $\text{BaFe}_{12-x}\text{Cr}_x\text{O}_{19}$  barium-chromium hexaferrite synthesis.

It is found that pretreatment of the reaction mixture in high-energy mills has a strong influence on its reaction capacity. Comparative data before and after treatment are presented. Mechanical activation decreases points of combustion initiation and maximum heat release, with exothermal effect of interaction getting significantly higher. Combustion wave for an activated charge mixture propagates 2.3-2.7 times faster than for a non-activated one. Herewith, combustion temperature is some lower and ferritization time is longer. Dependence of combustion parameters as a function of MA time is analyzed.

It is noted that MA influences not only on a phase composition of the combustion products but also on their formation mechanism. Relative importance of defect structure and specific surface for conversion completeness is discussed.

This work is supported by Russian and Belorussian Foundations for Basic Researches, grant RFBR 00-03-81193 Bel2000\_a, Russian Foundation for Basic Research, Grants RFBR 00-15-99054, 00-03-40141i.

## **O-2-146: The Effect of Melt Infiltration in High-Gravity Fields**

*V.N. Sanin, V.I. Yukhvid, A.G. Merzhanov*

*Institute of Structural Microkinetics and Materials Science*

*Russian Academy of Sciences, Chernogolovka, 142432 Russia*

To realize melt infiltration during SHS, the experiments were carried out in centrifugal machines. Using high gravity (up to 1000 g), we explored the effect of melt infiltration on the mechanism of SHS in multi-layer systems and also the possibility of obtaining ceramic-metal FGM with the graded content of metal binder. As objects of investigation, the  $\text{Cu}_2\text{O}-\text{Cu}-\text{Al}$  / (Ti - B), (Ti - B - Cr), (Cr - B) and  $\text{NiO}-\text{Ni}-\text{Al}$  / Ti - C two-layer structures were taken out. In the experiments liquid combustion products of upper layer saturated lower one. The rate of melt infiltration through lower pellet was changed upon variation load (from 1 to 1000 g). The average linear combustion velocity, the product chemical and phase compositions, their microstructures and distribution of concentrations along sample were determined.

The infiltration was found to markedly affect the burning velocity of lower (Ti - B, Ti - B - Cr, Cr - B and Ti - C) systems. Depending on green composition and load, the infiltration was either to full depth or partly. In the most cases, the samples obtained under load over 500g looks as monolayer. However, by following analysis was found that the samples have two-layer structure. The upper layer was alumina with rare inclusions of metal drops. The lower layer looks as composite structure consisting from metal matrix (Cu - Al, Ni - Al) and distributed  $\text{TiB}_2$ ,  $\text{CrB}_2$   $\text{TiC}$  drains. The matrix structure formed by selected infiltration of melted combustion products. The samples obtained under load low 500 g have not full saturation. A concentration gradient of metal binder (Cu - Al solution,  $\text{Ni}_3\text{Al}$ ) was formed. Besides, we carried out melt saturation through reacted pellet (when ignition was from bottom). Also, we analyzed some practical aspects of the centrifugal processes. The above technique was used to manufacture tube, functionally graded materials.

## **O-1-102: Electrophysic Peculiarities of SHS Processes in Metallic and Metal-Like Systems**

*A.I. Kirdyashkin, Yu.M. Maksimov, V.S. Korogodov, V.L. Polyakov, V.D. Kitler, V.V. Burkin*

*Department of Structural Macrokinetics of the Tomsk Scientific Center of Siberian Branch of Russian Academy of Sciences, Russia, 634021, Tomsk*

On the base of acoustic and plasma measurements it was stated that the propagation of SHS wave in metallic and hybrid systems is followed by the complex of inner physical phenomena, including characteristic generation of sound, and alternating electric fields in the frequency range more than 1 MHz, abnormal emission of charge carries, excitation of non-equilibrium power spectrum of electrons. The role of these phenomena is shown in SHS processes, including the realization of unheat mechanism of activation reaction, which, according to data obtained, allows to control the process effectively under conditions of application of external physical fields.

## **O-1-153: Evolution of Routes to Chaos in Condensed Phase Combustion with Melting**

*C.S. Raymond<sup>1</sup>, A. Bayliss<sup>2</sup>, B.J. Matkowsky<sup>2</sup>, V.A. Volpert<sup>2</sup>*

*<sup>1</sup>Department of Mathematics, University of Wisconsin - Madison  
Madison, WI 53706-1388, U.S.A.*

*<sup>2</sup>Department of Engineering Sciences and Applied Mathematics  
Northwestern University, Evanston, IL 60208-3125, U.S.A.*

We numerically study a model of condensed phase combustion with a melting reactant. For a fixed value of the melting temperature we increase a control parameter of the system, the Zeldovich number, and observe how the solution undergoes a series of bifurcations resulting in a chaotic behavior. The nature of the transition to chaos depends on the value of the melting temperature. For high melting temperatures (more specifically, when melting occurs in the reaction zone) the transition proceeds through a series of period doubling and period halving bifurcations followed by an intermittent behavior, in agreement with previous results. For low melting temperatures (i.e., when melting occurs far ahead of the reaction front) the transition is due to a direct period doubling route, which was previously observed in a model without melting.

The main goal of this paper is to understand how one route to chaos transforms into the other route as the melting temperature is varied between the two extremes. By performing computations for intermediate melting temperatures we are able to partition the melting temperature – Zeldovich number parameter plane according to different behaviors of the solution. Such a map demonstrates how one route to chaos evolves into another. We find, in particular, several interesting solution behaviors, such as bistability between a branch of singly periodic solutions and a period doubling cascade, an interval of chaotic solutions, and an inverse cascade.

## **O-1-129: Experimental and Theoretical Study of Solid Product Microstructure Formation during SHS**

*A.S. Rogachev<sup>1</sup>, S.A. Kirillov<sup>2</sup>, I.M. Kotin<sup>3</sup>*

*<sup>1</sup>Institute of Structural Macrokinetics and Materials  
Science, RAS, Chernogolovka, Moscow Region, 142432 Russia*

*<sup>2</sup>Research Institute of Physical Chemical Problems, Belorussian State University, Minsk,  
Belarus*

*<sup>3</sup>Institute of Technical Acoustics, Vitebsk, Belarus*

Mechanism of the solid product microstructure formation remains one of unsolved problems in SHS. In the present work, we suggest simplified model based on the assumption that solid reactant particles directly dissolve into the melt of other reactant, and solid product crystallizes randomly in the volume of the melt. No continuous layer of the product forms at the inter-reactant boundaries. Previous experimental study of microstructure of primary solid products shown that proposed mechanism may be responsible for the microstructure formation in many SHS-systems, such as Ti-C, Ti-B, Ni-Al, and others. Mathematical model built on this assumptions allow us to

establish correlation between size distribution of the initial reactant particles and size distribution of the product crystals appeared during the SHS reaction. Experimental study of the particle size distribution was proceeded using combustion wave quenching method, as well as particle - foil model technique. Images of microstructures were digitized and treated by computer in order to obtain statistically proved numerical characteristics of the product grains. Theoretical model considered the process of microstructure formation as evolution of cellular structure, where each cell represented one of possible solid or liquid phases. The state function of the cellular structure was defined. This function have a lot of variables. One part of variables is responsible for geometrical characteristics of a cell: a volume, the boundary structure. The other part of variables defines the neighborhood characteristics. The main kinetic equation describing the evolution of the given state function is obtained. It is equivalent to the evolution equation of cellular structure. Different approaches to obtain analytical solutions of the main kinetic equation are considered. The analysis of the classes of state functions of the cellular structure is performed. Bundle cellular automata demonstrating the evolution of the cellular structure on micro level are built on the basis of the main kinetic equation. The analysis of the kinetics of structure elements of interfaces is made. Finally, the comparison of the theoretical results with the experimental data shows reasonable correlation between them.

This work is supported by Russian and Bielorussian Foundations of Basic Researches, grant RFBR 00-03-81165 Bel2000\_a.

#### **O-1-197: Fabrication of Ceramic-Metal Layered Composites by SHS/QP**

*Z.Y. Fu, W.M. Wang, H. Wang, Q.J. Zhang, R.Z. Yuan*

*State Key Lab of Advanced Technology for Materials Synthesis and Processing*

*Wuhan University of Technology, Wuhan 430070, P. R. China*

SHS plus quick pressing (termed SHS/QP) was used to produce ceramic/metal layered composites. The temperature and stress distribution in the sample in the periods of reaction, densification and cooling were analyzed theoretically. It is concluded that the sintering can be carried out with temperature difference, because the ceramic side will give out more heat, which results in an expected better stress distribution in the densified sample. Experiments proved the theoretical analysis.

#### **O-1-190: Features of Compaction Kinetics of Powder Materials in Nonisothermal Conditions**

*L.S. Stelmakh<sup>1</sup>, A.M. Stolin<sup>2</sup>*

*<sup>1</sup>Institute of Problems of Chemical Physics Russian Academy of Sciences*

*<sup>2</sup>Institute of Structural Macrokinetics and Materials Science, Russian Academy of*

*Sciences, Chernogolovka, Moscow Region, 142432, Russia, E-mail: [stelm@ism.ac.ru](mailto:stelm@ism.ac.ru)*

The new features of a nonisothermal kinetics of compaction are established, which are characterized by the following main facts: 1) the presence of an induction period, during which the compacting does not take place practically; and 2) the capability of "explosive" nature of compaction. The carried out numerical calculations have allowed to update a picture of compacting and to dedicate two autonomous processes in a wave mode: propagation of a compression area along a sample from a layer to layer and compacting of a material in a compression area. It is shown, that at increase of an altitude of a compressed sample there is a continuous transition from a regular mode of compaction to a wave one.

On the basis of a numerical solution of a problem about nonisothermal compaction and cooling of a viscous compressible media in the cylindrical chamber, the analysis of influencing of the thermal factors and geometrical sizes of a sample on characteristic times of two autonomous processes is conducted: spatial propagation of a compression area along a sample from a layer to layer and temporary extracompacting of a material in the compression area. It is revealed, that the effect of slowing the induction period down is increase with remoteness of cross-section of a sample from

the migrating cylinder piston and conditions impairment of a thermal insulation of a sample ends. The known earlier experimental result about the presence of two critical sizes of a sample determining condition for obtaining poreless materials is affirmed and justified.

### **O-2-182: Gravity-Induced Effects in SHS**

*H.E. Grigoryan, A.S. Rogachev, A.E. Sytschev, S.E. Zakiev*

*Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences, Chernogolovka, Moscow region, 142432 Russia, tel.: (095) 962-80-35, e-mail: [sytschev@ism.ac.ru](mailto:sytschev@ism.ac.ru)*

Formation of high-porosity and foam materials is closely associated with combustion-induced expansion of substance. In this work, we determined the real burning velocity (with respect to motionless starting mixture) and examined the dynamics of sample expansion or shrinkage.

Experiments carried out in vacuum allowed us to measure total gas evolution ( $V$ ) and calculate specific gas evolution ( $v$ ) for each particular mixture. The dynamics of sample deformation was found to depend on  $v$ , green structure, and ambient gas pressure ( $P$ ). The amount of released gases (largely, hydrogen) strongly decreases with increasing size ( $d$ ) of reactant particles. For combustion in Ar, the relative sample elongation ( $\varepsilon$ ) was found to strongly depend on ( $v, d$ ) for  $d < 80 \mu\text{m}$ , that is, for  $v = 0.9\text{--}1.8 \text{ mmol/g}$ . For larger particles,  $\varepsilon$  undergoes saturation at some level (about 13 %), despite further decrease in  $v$ . In vacuum, the  $\varepsilon(v)$  dependence is steeper.

Our data suggest that the gas pressure in pores sharply increases within the combustion wave and then rapidly decreases due to infiltration of evolved gases into the environment. When the total amount of evolved gases is sufficient to increase the gas pressure in pores up to several tens of atmospheres, the true value of expanding pressure attains values of only tenths to hundreds atmospheres.

It may be assumed that gravity forces manifest themselves largely at contacts between reagent particles. Their action can be expected to be most pronounced during melting and in the presence of liquid phase, that is, in the zone of combustion.

This work was supported by the Russian Foundation for Basic Research (project no. 01-03-32077).

### **O-1-163: High-Pressure Bulk Nitridation of Transition Metal Elements by Combustion**

*A. Martinelli, M. Ferretti*

*Dipartimento di Chimica e Chimica Industriale*

*Via Dodecaneso 31 – 16146 Genova, Italy*

Transition metal plates (Ti, V, Nb, Cr) were nitrided by means of the chemical oven technique under high nitrogen pressure (up to 700 bar). Nitridation was carried out in the reaction chamber of a high pressure-high temperature autoclave and the reaction was ignited by means of a Cu-coil connected to a high power generator. Reaction products were characterized by means of XRD analysis, OM and SEM observation after metallographic preparation. Thick nitrided films grew on the surfaces of the metal plates in a time of a few seconds. The phase sequence inside the nitrided plates is the same reported in the respective binary phase diagrams at high temperature, with respect of the possible phase transformations occurring during cooling. In general the mono-nitride  $\text{MetN}_{1-x}$  constitutes the external layer and the solid solution  $\text{Met}(\text{N})$  the core of the sample. The phase sequence inside the nitrided samples may be summarized as follows, from the surface towards the center of the plate: nitrided Ti-plates:  $\delta\text{-TiN}_{1-x}$ ,  $\varepsilon\text{-Ti}_2\text{N}$ ,  $\alpha\text{-Ti}(\text{N})$ ,  $\beta\text{-Ti}(\text{N})$  transformed into  $\alpha\text{-Ti}(\text{N})$ ; nitrided V-plates:  $\delta\text{-VN}_{1-x}$ ,  $\beta\text{-V}_2\text{N}_{1-x}$ ,  $\alpha\text{-V}(\text{N})$ ; nitrided Nb-plates:  $\delta\text{-NbN}_{1-x}$ ,  $\gamma\text{-Nb}_4\text{N}_{3\pm x}$ ,  $\beta\text{-Nb}_2\text{N}_{1-x}$ ,  $\alpha\text{-Nb}(\text{N})$ ; nitrided Cr-plates:  $\delta\text{-CrN}_{1-x}$ ,  $\beta\text{-Cr}_2\text{N}_{1-x}$ , a two-phase layer characterized by a pearlitic structure originated from a melt,  $\alpha\text{-Cr}(\text{N})$ . The reaction that leads to the nitridation of the metal plates is of the solid-gas type; nitrides grow by inward reactive diffusion of

nitrogen towards the center of the sample. No massive melting phenomenon occurs during combustion.

The lattice parameter of  $\text{MetN}_{1-x}$  strongly depends on the nitrogen pressure applied during combustion. This is due to the fact that most transition metal nitrides are characterized by wide homogeneity ranges; as a consequence different synthesis conditions lead to the formation of nitrides with different nitrogen content and hence different properties.

### **O-3-139: High-Resolution Time-Resolved X-ray Diffraction Studies of SHS Reactions in an External Magnetic Field**

*Q. A. Pankhurst<sup>1</sup>, L. Affleck<sup>1,2</sup>, H. Spiers<sup>2</sup>, I.P. Parkin<sup>1</sup>, M.V. Kuznetsov<sup>1,3</sup>,  
E. Kvick<sup>4</sup>, A. Terry<sup>4</sup>, G.B. Vaughan<sup>1</sup>*

<sup>1</sup>*Department of Physics, University College London, Gower Street, London WC1E 6BT, U.K.*

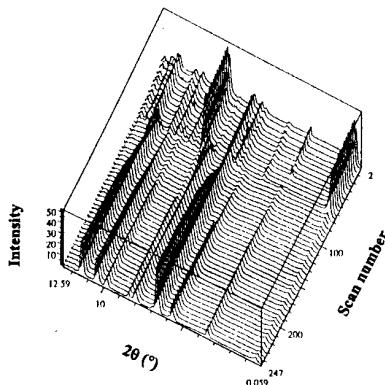
<sup>2</sup>*Department of Chemistry, University College London, 20 Gordon Street London WC1H 0AJ, U.K.*

<sup>3</sup>*Institute of Structural Macrokinetics and Materials Science, Chernogolovka Moscow Region, 142432, Russia*

<sup>4</sup>*European Synchrotron Radiation Facility, Grenoble F-38043, France*

A set of high-resolution time-resolved X-ray diffraction experiments have been undertaken on the Materials Science beamline, ID11, at ESRF. X-ray diffraction patterns were recorded at a rate of one every 110 ms, comprising 50 ms exposure time and 60 ms readout time

from a  $1024 \times 1024$  pixel FREION CCD camera. Excellent counting statistics were obtained, as illustrated in the figure at right, which plots every fifth scan recorded from an SHS reaction of  $\text{MgO}$ ,  $\text{ZnO}$ ,  $\text{Fe}$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{NaClO}_4$  to form the magnesium ferrite product  $\text{Mg}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ . Detailed inspection of the data revealed many features reflecting the nature of the combustion process. These ranged from relatively slow changes, such as peak shifts due to lattice contraction of the product phases on cooling, through to relatively fast transients, which are most likely evidence of momentary macroscopic restructuring in the powder as the combustion wavefront passes. These results will be discussed, along with the results of a series of experiments comparing the nature of the SHS process in powders in zero field, in a weak magnetic field ( $\sim 200$  mT) and in a strong magnetic field ( $\sim 1.1$  T).



### **O-3-73: In Situ Synthesis of Oxide Ceramic Matrix Composites (CMC's) Based on Powder**

#### **Blends of Fly Ash with Magnesium and Aluminum**

*I. Gutman<sup>1</sup>, I. Gotman<sup>1</sup>, M. Shapiro<sup>2</sup>*

<sup>1</sup>*Faculty of Materials Engineering, Technion, Haifa 32000, Israel*

<sup>2</sup>*Laboratory of Transport Processes in Porous Materials Faculty of Mechanical Engineering, Technion, Haifa 32000, Israel*

Fly ash is the by-product of coal-fired power stations and constitutes a major ecological hazard. The disposal of fly ash causes significant economical and environmental problems. As a result power plants sell fly ash at very low prices. Over the past decade much research has been put in order to improve utilization of fly ash, however most of its consumption still relies on construction processes. Although construction processes utilize huge amounts of fly ash it is still less than 20% of the amount generated. This is the main reason that researchers are searching for alternative

routes in order to increase consumption of fly ash.

Self-propagating High-temperature synthesis (SHS) could be a convenient means of utilizing fly ash as a reagent for the production of other materials. This method could generate more stable products for broad applications.

Fly ash consists mainly of oxides:  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  (most of it as mullite  $2\text{SiO}_2\text{Al}_2\text{O}_3$ ) as major phases, while other oxides ( $\text{CaO}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$  etc.) and salts are present at much lower concentrations. Many of the phases will exothermically react with some metals and therefore the blend can serve as an SHS reagent.

In this research we used fly ash blended with Mg, Al and in some cases additional fine powders in order to synthesize oxide based ceramic matrix composites (CMC). Thermal explosion (TE) experiments were carried out, however resulted in highly porosive products. In order to increase final density TE experiments were preformed under pressure. Furnace temperatures used in order to initiate the reaction were as low as  $750^\circ\text{C}$ . Analyses by X-ray diffraction (XRD) and scanning electron microscopy with chemical analysis (SEM/EDS) showed that the reaction resulted in the formation of two main phases: Spinel ( $\text{MgAl}_2\text{O}_4$ ) and  $\text{MgO}$ . More complicated intermetallic phases on the basis of Al-Fe-Si sometimes with Ca and Ti were also formed. Spinel phase, which is the matrix phase, is stable at temperatures as high as  $1900^\circ\text{C}$  and  $\text{MgO}$  remains stable at higher temperatures. This system therefore has a potential to produce refractory oxide CMC's, that combine exceptional hardness with excellent oxidation resistance.

#### **O-1-130: The Laws of Activated Combustion Front Propagation in $\text{SiO}_2\text{-Al-C}$ System at Directed Gas Infiltration**

*L.S. Abovyan<sup>1</sup>, H.H. Nersisyan<sup>1</sup>, S.L. Kharatyan<sup>1</sup>, R. Orrù<sup>2</sup>, G. Cao<sup>2</sup>*

*<sup>1</sup>Nalbandyan Institute of Chemical Physics NAS of Armenia, 375044, Yerevan, Republic of Armenia*

*<sup>2</sup>Dipartimento di Ingegneria Chimica e Materiali  
Università degli Studi di Cagliari, Piazza d'Armi  
09123, Cagliari, Italy*

In actual practice SHS reactions are followed by certain gas evolution. The basic sources of gases are initial powders, containing adsorbed gases and high-volatile impurities, as well as various organic and inorganic additives [1] used as combustion promoters (hydrocarbonaceous and halogen-containing polymers, nitrogen-containing substances, hydrides of metals, etc.). As a rule, the degassing process affects the combustion velocity and the morphology of final products too. Consequently, this process is of more direct interest when solving the synthetic problems.

In the present work the laws of gas evolution are investigated at activated combustion of  $3\text{SiO}_2\text{-}4\text{Al-3C}$  system, as well as their influence on the morphology of products synthesized.

By application of microthermocouple technique combustion laws in the  $3\text{SiO}_2\text{+4Al+3C}$  mixture are investigated under the conditions of counter-current and co-current (forward) infiltration of gases allocated at combustion. Two sources of gas evolution were used: teflon and polystyrene. It is shown that when replacing a small part of soot by polytetrafluoroethylene (up to 4 wt.%) the dynamics of combustion velocity change along the sample is different and depends on the direction of gas infiltration. At counter-current infiltration mode the combustion wave propagates with a constant velocity, while at co-current infiltration the combustion velocity has a strongly increasing character. The addition of polystyrene to the initial mixture stabilizes the front propagation. It is established that the stabilization effect is caused by polystyrene decomposition before the combustion front and appearing the additional porosity in the direction of combustion front propagation.

The experiments have shown that gas generating additives influence not only on combustion parameters, but on the morphological characteristics of final products as well. In particular, it was found out that under the co-current infiltration mode thread-like SiC crystals are formed in the direction of gas flow from the burning sample.

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### O-1-162: The Local Ignition of a Solid by the Heat Beam, Both Fixed and Moving across the Surface

*A.D. Margolin, V.G. Krupkin, V.S. Posvianskii*

*Semenoff Institute of Chemical Physics, Russian Academy of Sciences*

*4 Kosygina str., Moscow, 119991, Russia*

The most studied was the one-dimensional ignition of the half-space of a solid (SHS-systems, powders, explosives) by a thermal flow (steady or variable with time) or a hot plate. Also, the studies were conducted with local ignition of a solid on heating a spot on the flat surface. For this case, calculations were performed with using non-steady-state two-dimensional models.

The first part of the present contribution is devoted to the spherically symmetric ignition by thermal beam. This beam is applied to the surface of a hemispherical hollow (deepening) at the surface of the solid being ignited. Replacing the heated flat spot by heated depending enables one to reduce the two-dimensional problem to the one-dimensional one. The consideration of the problem as being both high-symmetry and one-dimensional has ensured that it has been solved over a wide range of starting parameters. Limiting conditions and times of ignition have been found as a function of both intensity of the thermal beam and its diameter, as well as of heat and kinetic parameters. Interpolated formulae have been found, describing results of the numerical solution with an accuracy of 1% or better.

In the second part, limiting conditions of the local ignition of a solid by the radiation beam have been found when the hot spot moves across the solid surface. In such a case, the criterion for ignition is a function of width and intensity of the beam, the rate of its moving, as well as of heat and kinetic parameters of a solid. The results of calculations are given both in tabulated and graphical forms.

### O-3-72: Macrokinetic Laws of Activated Combustion of Silicon-Nitride-Based Composite Powders

*H.L. Khachatryan, H.H. Nersisyan, S.L. Kharatyan*

*Nalbandyan Institute of Chemical Physics NAS of Armenia, 375044, Yerevan*

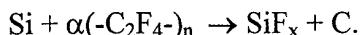
*Republic of Armenia*

The powders of silicon nitride based composites ( $\text{Si}_3\text{N}_4$ -SiC,  $\text{Si}_3\text{N}_4$ -TiN,  $\text{Si}_3\text{N}_4$ - $\text{MoSi}_2$ , etc.) are of great importance for the modern ceramic industry. It is well known that combining the silicon nitride with refractory inorganic compounds causes the raise of the operational characteristics of ceramic materials. The self-propagating high-temperature synthesis (SHS) is acknowledged to be one of the most progressive methods for synthesis of these powders. According to the literary data, a number of composite powders, including silicon nitride based ones have been already produced by this method.

The present work is devoted to investigations of macrokinetic laws of synthesis of silicon nitride based composites under the activate combustion mode. Our long-standing investigations in the field of synthesis of transition metal carbides have shown, that the use of combustion promoters allows to control the mechanism of chemical reactions and the microstructure of products obtained [1].

Combustion in  $\text{Si-C-N}_2$ ,  $\text{Si-Me}(\text{Ti,Mo})-\text{N}_2$  systems in the presence of activate additives was studied at nitrogen pressures 1-5 MPa. Various organic and inorganic compounds, including polytetrafluoroethylene (teflon), nitrates of alkaline metals and ammonium, nitrogen-containing organic compounds were used as additives. Microthermocouple studies have shown that in the majority of cases the combustion wave in these systems has a double-stage structure. The first stage, as a rule, is the leading one, where primarily the interaction between the silicon and

combustion activator takes place. In particular, when using teflon, the interaction is described by reaction:



The temperature for this stage makes about 1370-1470 K when  $\alpha < 0.1$ .

The formation of silicon nitride and carbide phases as well as the accompanying substances proceed in the second stage of the process where the combustion temperature can reach 2300 K. SEM analyses allowed to establish that the promoters used not only intensify the combustion process, but change substantially the phase composition and the morphology of final products as well. In particular, there appear thread-like crystals and whiskers of  $\text{Si}_3\text{N}_4$  in the final products, and the portion of low-temperature  $\alpha\text{-Si}_3\text{N}_4$  phase increases considerably. The particles size of composite powders, synthesized under these conditions, averages between 1 and 2  $\mu\text{m}$ .

The work is supported by the US Civilian Research and Development Foundation (CRDF Grant No. AC2-2051) and INCO-Copernicus-2 (Contract No. ICA2-CT-2000-10020).

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### O-1-3: Magnetic and Electric Fields Produced by SHS

*D. Luss<sup>1</sup>, M. D. Nersesyan<sup>2</sup>, J. R. Claycomb<sup>1</sup>, J. T. Ritchie<sup>1</sup>, J. H. Miller, Jr.<sup>1</sup>, J. T. Richardson<sup>1</sup>*

<sup>1</sup>*University of Houston, Houston, TX 77204-4792, USA*

<sup>2</sup>*Institute of Structural Macrokinetics and Materials Science, Chernogolovka, 142432, Russia*

Magnetic and electric fields were generated by various SHS-reactions producing various materials. Transient electric fields of up to 1.5V were during the high-temperature oxidation of pure metals either by gaseous oxygen or by solid peroxides or perchlorates. The shape, sign and magnitude of the induced temporal electric signal depended upon the reactant properties, reaction mechanism, and mode of the front propagation and mobility of the ions formed. Low-level transient magnetic fields (order of nT) were measured by superconducting quantum interference devices (SQUIDs) during the synthesis of both non-ferromagnetic and ferromagnetic compounds. The permanent magnetic field formed by the synthesis of ferromagnetic materials (ferrites) depended on the difference between the combustion temperature and the Curie temperature of the product.

Two qualitatively different types of magnetic signals were observed during the combustion of pure metal and metal/metal-oxide powders in oxygen. The combustion of Nb, Cr and Co in oxygen generated a slowly oscillating field, while the combustion of Zr, Hf, Mn, Ti, Mg and Fe generated a slowly oscillating field on which rapid oscillations were superimposed. The magnetic field oscillations are most probably generated by electrical current fluctuations. A simple electromagnetic model predicts the qualitative features observed in the experiments.

The work is supported by the NSF Grant #CTS-0003015

### O-2-175: Mechanism of the SHS Reaction $\text{Nb} + \text{Al} \rightarrow \text{NbAl}_3$ Using Synchrotron TRXRD

#### Experiments Coupled with Infrared 2D Observations

*V. Gauthier<sup>1</sup>, J.P. Larpin<sup>1</sup>, E. Gaffet<sup>2,4</sup>, D. Vrel<sup>3,4</sup>, F. Bernard<sup>1,4</sup>*

<sup>1</sup>*LRRS, UMR5613 CNRS – Université de Bourgogne - BP , 47870 21078 Dijon, France*

<sup>2</sup>*Far from Equilibrium Transitions Phases Group, CNRS UMR , 5060 90010 Belfort, France*

<sup>3</sup>*LIMHP, UPR 1311 CNRS, 99 Av. J.-B Clément, , 93430 Villetaneuse, France*

<sup>4</sup>*GFA, GDR 2391 CNRS – Université de Bourgogne - BP , 47870 21078 Dijon, France*

Nanostructured niobium aluminides ( $\text{NbAl}_3$ ) were synthesized using an alternative route so - called MASHS [1,2]. This original process combines a short duration ball milling (MA) with a self-

sustaining combustion (SHS). The microstructure evolution of the powder mixture during mechanical activation step was monitored using XRD profile and SEM investigations. Short duration ball milling of (Nb+3Al) powders produces Nb and Al nanocrystallites into micrometric particles. After a cold-compaction of the mechanically activated mixtures, the exothermic reaction between reactant powders is initiated by an external heat source and becomes self-sustaining to yield the final product. It was demonstrated that pure NbAl<sub>3</sub> with nanometric structure could be produced via successive combustion fronts.

In order to understand the mechanism of the NbAl<sub>3</sub> formation, an original experiment was designed to study in-situ the formation of NbAl<sub>3</sub> phase in each combustion front. The synchrotron TRXRD experiments coupled with a 2D infrared camera were performed to monitor the structural and the thermal evolutions. Owing to the temporal resolution of 100ms between two consecutive diffraction patterns, it was possible to observe several steps before obtaining the niobium aluminides compounds. Owing to the temporal resolution of 100ms between two consecutive IR images, it was possible to observe 6 constitutive combustion fronts which propagate with increasing velocities.

A synchronization (spatio-temporal) between these two data (XRD and IR) allows to determine the mechanism of the SHS reaction Nb + 3Al → NbAl<sub>3</sub>. Indeed, it can be shown that the mechanism of this reaction corresponds to a heterogeneous reaction in the liquid phase. The germination of the NbAl<sub>3</sub> compound was occurred on the surface of Nb solid which is located in the Al(Nb) liquid phase.

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#### ✓ O-2-53: Microstructural Investigation of SHS Produced Zirconium Diboride

*S.K. Mishra(Pathak), S. Das, S.K. Das, P.Ramchandrarao*

*National Metallurgical Laboratory, Jamshedpur- 831007, India*

*Fax: 91-0657-270527, E mail : [suman@csnml.res.nic.in](mailto:suman@csnml.res.nic.in)*

Zirconium diboride is emerging as a potential advanced ceramic material due to its high melting temperature, hardness, elastic modulus and electrical conductivity, excellent chemical resistance to HCl, HF and various non-ferrous metals, cryolite and non-basic slags. These excellent properties make ZrB<sub>2</sub> an important material for uses at high temperatures requiring high resistance to wear, high temperature oxidation and corrosion.

Several techniques are known in literature to prepare zirconium diboride powders. The different techniques are : from elements by melting, sintering or hot pressing, borothermic reduction of metal-oxides and boric oxide, reduction of the metal oxide with carbon or boron carbide, aluminothermic, magnetiothermic and silicothermic reduction of metal oxide mixture and self propagating high temperature synthesis (SHS) synthesis from elemental powder of boron and zirconium.. SHS process takes the advantage the exothermic reactions to form the advanced materials. The essential feature of the process is that the heat required to drive the chemical reaction is supplied from the reaction itself. In recent years the SHS process has found applications for preparing intermetallics and advanced high temperature materials particularly carbides, borides, silicides and nitrides<sup>1,2</sup>. Advantages, fundamental and technological aspects of SHS have been reviewed in literature<sup>3,4</sup>. Owing to the high cooling rates and high defect concentrations non-equilibrium metastable structures are expected to exist in the SHS produced powders, resulting in more reactive and enhanced sinterability of the powders<sup>5</sup>. It is observed that in all the above processes, the time requirement is more and it requires high temperatures in the range of 2000 to 2200°C to achieve 95% and above pure products or pure elemental powders are required as starting raw material which make the process costly. In the present investigation, zirconium diboride powder

is prepared by using cheaper raw materials such as oxides and salts of zirconium and boron. The prepared SHS powder is found to have 95 % purity.

Due to inherent nature of the SHS process the microstructures of the SHS product are found different than conventional ones. Microstructures are very important, which ultimately tailor the strength and physical properties of the material. However, there is not much report available on microstructures of zirconium diboride prepared by SHS process. In the present investigation a detailed studies on the microstructure of as produced zirconium diboride powder and the microstructure development in the sintered product has been carried out by scanning and transmission electron microscopy. A study on defect structures, grain boundary interface and defects in the as prepared powders will be discussed.

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### O-2-218: Microstructure and Mechanical Properties of IN-SITU NiAl-Based Composites Strengthened by TiC

*J.T. Guo, C.Y. Cui, G.S. Li, D.T. Jiang*

*Institute of Metal Research, Chinese Academy of Sciences, Shenyang, 110016, PR China*

Self-propagating high-temperature synthesis (SHS) is a term applied to the formation of certain compound by using strongly exothermic reactions between powder constituents. Several NiAl-based composites, including NiAl-Ti-TiC, NiAl-Al<sub>2</sub>O<sub>3</sub>-TiC and NiAl- Cr(Mo)-TiC, have been fabricated by hot pressing aided exothermic synthesis (HPES) plus hot isostatic pressing (HIP).

In NiAl-Ti-TiC composite, there exists a large amount of Heusler particles that distribute regularly in NiAl grains and TiC particles have a tendency to reside on the grain boundary. The composite shows very high strength even at high temperatures but little ductility at low temperatures. Both the improved strength and limited ductility can be related to the needle like Heusler precipitates. The incorporation of TiC particles is beneficial to the ductility.

As to NiAl-Al<sub>2</sub>O<sub>3</sub>-TiC composite, the adiabatic temperature and liquid-phase content for the reaction system were examined, where the adiabatic temperature increases with increasing ignition temperature and reinforcement content. The particles tend to accumulate at the grain boundary, some small TiC particles were found to exist in Al<sub>2</sub>O<sub>3</sub> particle and a model is proposed to explain this observation. The strength of the composite is superior to the binary NiAl; however, it decreases rapidly at high temperature.

In NiAl-Cr(Mo)-TiC composite, TiC particles prefer to reside on the grain or phase boundaries, the size of these particles are larger than those existing in the NiAl grains. Its elevated temperature compressive behavior was investigated. The flow stresses of the composites generally decreased with increasing temperature and /or decreasing initial strain rate. It was found that the deformation feature of the composites could be adequately described by power-law equations. The strengthening mechanisms are also discussed preliminary.

It is concluded that the strength of *in-situ* NiAl-based composites by HPES processing can be effectively improved.

**Key words:** HPES, NiAl-based composite, the adiabatic temperature, mechanical properties

**Corresponding author:** Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, P.R.China, Fax:+86-24-23891320, Email: jtguo@imr.ac.cn

## O-2-51: Microstructure Formation Mechanism of $TiO_2$ - $B_2O_3$ -Mg System during Combustion Synthesis

Weimin Wang,<sup>1</sup> Zhengyi Fu, Hao Wang, Runzhang Yuan

State Key Lab of Advanced Technology for Materials Synthesis and Processing

Wuhan University of Technology, Wuhan 430070, P.R. China

$TiB_2$  ceramic has excellent physico-chemical properties such as high hardness, good corrosion resistance, good wear-resistance and excellent electricity conductivity, which make  $TiB_2$  materials have a great wide application areas as advanced engineering ceramics. Combustion synthesis method has been used to fabricate the  $TiB_2$  ceramic from  $TiO_2$ - $B_2O_3$ -Mg system, but the research literature concerned microstructure formation mechanism was few.

In this paper, Thermal analysis methods (TG--DTA) and x-ray diffraction methods were employed to reveal the chemical reaction processes occurred during combustion synthesis. Results showed that gasification loss of metal reducer Mg could be found, which caused the rise in impurity phase. The content of metal Mg in reactant mixture has a great influence on the mineral phases of synthesised product. The main impurity  $3MgO \cdot B_2O_3$  decreases remarkably with increases of metal Mg.

CFQ (Combustion Front Quench) method was used to obtain the microstructure characterised zones during materials structure formation processes from reactant mixture to synthesised product. SEM and EDS were used to study the mechanism of structure formation. Results showed that during combustion synthesis of  $TiO_2$ - $B_2O_3$ -Mg system,  $B_2O_3$  melted and covered uniformly around Mg and  $TiO_2$  particles; element Mg diffused into molten  $B_2O_3$  and reacted with  $B_2O_3$  to form element Boron and richer Boron compound  $MgB_2$  according to chemistry reactions:  $B_2O_3 + Mg \rightarrow B + MgO$  and  $B_2O_3 + Mg \rightarrow MgB_2 + MgO$ , while  $TiO_2$  reacted with Mg to form element Titanium and MgO. Nanometer scale  $TiB_2$  microcrystalline was formed by chemistry reaction between Ti and B or  $MgB_2$ . And then,  $TiB_2$  microcrystalline grew quickly under high combustion temperature.

**Key words:**  $TiB_2$ ,  $TiO_2$ - $B_2O_3$ -Mg system,  $TiB_2$  microcrystalline, mechanism of structure formation

<sup>1</sup>**Corresponding author:** Wang Weimin, E-mail:wangwm@hotmail.com

## O-2-154: Microwave SHS Synthesis of Silicon Carbide Submicron Powders

T. Chudoba<sup>1</sup>, D. Kuzmenko<sup>1</sup>, A. Presz<sup>1</sup>, W. Lojkowski<sup>1</sup>, J. Binner<sup>2</sup>, T. Cross<sup>3</sup>

<sup>1</sup>High Pressure Research Center, Polish Academy of Sciences

Sokolowska 29, 01-142 Warsaw, Poland. POBox65

Phone +48 22 6324302, Fax +48 22 6324218 or +48 3912 0331

<sup>2</sup>IPTME, Loughborough University, Loughborough, Leicestershire, LE11 3TU, UK

<sup>3</sup>School of Electrical & Electronic Engineering, University of Nottingham

University Park, Nottingham NG7 2RD, UK

SHS - Self-propagating High-temperature Synthesis is a technology of producing ceramic and intermetallic powders where the exothermic reaction once started propagates in a self-sustaining mode through the reaction batch. The exothermic reaction  $Si + C \rightarrow SiC$  once started propagates in a self-sustaining mode through the reaction batch. In the conventional reaction, the batch of substrates must be heated to a temperature of at least 1200 K before the once ignited reaction propagates. In practical applications, the batch of substrates is heated up to the melting point of silicon where the reaction takes place in the form of combustion synthesis. This procedure induces difficulties as far as controlling the product uniformity and grain size.

We have shown that using a special microwave reactor with well-defined hot spots distribution for the ignition of the Si and C gives additional flexibility for controlling the reaction. Proper positioning of the hot spots in relation to the batch of substrates permitted us to optimize the place of ignition and better control the reaction propagation. As a final consequence, the fraction of nanocrystalline powders in the reaction product could be maximized.

Furthermore, our results indicate that the ignition reaction is caused by high electric field gradients at Si-C interfaces. The above results follow from systematic studies of the effect of composition of the reaction mixture on the ignition process and on the microstructure of the products.

It follows that specific microwave effects lead to improved microstructure of SiC powders produced during the MW-SHS process.

#### **O-1-50: Modeling of Nonstationary Combustion Wave in Heterogeneous Systems**

*A.G. Merzhanov<sup>1</sup>, P.M. Krishenik<sup>2</sup>, K.G. Shkadinskii<sup>2</sup>*

*<sup>1</sup>Institute of Structural Macrokinetics and Material Science Problems Russian Academy of Sciences, Chernogolovka, Moscow Region, 142432 Russia*

*<sup>2</sup>Institute of Problems of Chemical Physics, Russian Academy of Sciences Chernogolovka, Moscow Region, 142432 Russia*

The experimental data was obtained in recent years require going beyond the scope of the quasi-homogenous approach and developing basic principles for describing discrete combustion waves. In this work mathematical model is suggested for the analysis of the nonstationary processes occurring in exothermic reactions during propagation of the wave front in the layer-by-layer heterogeneous systems.

Alongside with limiting modes of combustion- quasi-homogenous and relay combustion conditions, the intermediate regimes are investigated. The limiting sizes of layers for existence of quasi-homogenous modes of combustion are determined. It was shown that than the heterogeneity scale is less than width of "homogenous" zone of reaction, the combustion front has homogenous structure. The features of the wave combustion, caused by discrete structure of homogeneous system, are investigated.

Dynamics of transition from quasi-homogenous mode of combustion to relay combustion was analyzed. It was shown that in intermediate region the temperature in the zone of reaction essentially exceeds equilibrium temperature of burning. The combustion wave propagation of flame is characterized relaxation oscillations of all characteristics front, including velocity flame. The period of fluctuations is determined by a long stage of heating of reacting medium, in which the next reacting plate behaves in a mode of dynamic thermal explosion. In a considered regimes in each reactionary layer the spatial distribution of temperature can be neglected. The structure of the flame supposes the simplified description in frameworks of "discrete" model.

For larger layers, when the heterogeneity scale exceeds characteristic size of combustion wave, the system conversion in a relay combustion conditions. It was find the dynamic characteristics of the relay combustion of such systems and show that the temperature in reaction zone exceeds the adiabatic temperature of combustion.

For the first time was received, that the maximal velocity is achieved on the certain intermediate level of sizes of layers.

#### **O-3-204: The Preparation of Nano-sized Oxides by Chemical Pyrolysis from Precursors**

**Produced by Soft Chemistry**

*P. Pramanik*

*Department of Chemistry, Indian Institute of Technology, Kharagpur 721302, India*

The paper presents the state of art of the synthesis methods suitable for the preparation of nano-sized particles of ceramic oxides through chemical pyrolysis. Three precursor solution based preparative methods that have been developed are discussed. The methods involve evaporation/flame pyrolysis of a polymer/complex based precursor solution. The precursor solutions are constituted of the desired metal ions dispersed in a polymeric reagent or, metal ions complexed with a chelating agent or, metal-ligand complex dispersed in a polymeric reagent. The polymeric reagent used are Polyvinyl alcohol (PVA) or, Sucrose in presence of 10 mole% of PVA while the chelating agents include organic amines such as Diethanolamine (DEA) and

Triethanolamine (TEA) and organic acids such as Citric/Oxalic/Tartaric acid. The polymeric reagents/ the chelating agents used in the precursor solution play a dual role. They help to keep the metal ions uniformly distributed through out the viscous liquid at the time of evaporation and thus circumvent the precipitation /segregation of the metal ions from solution. Again, the carbonaceous materials, obtained from the evaporation of the polymer/chelating agents, provide heat through combustion for the formation of the respective phases. This facilitates the reduction of the external temperature required for the formation of the desired mixed oxide phase. Rapid evaporation of the entire precursor solution results in a voluminous mass rich in mesoporous-carbon pyrolysis of which yields the fine oxide powders. The exothermic decomposition/pyrolysis of the precursor powders is accompanied by the evolution of large amounts of gases. The evolution of various gas (such as: water vapour, CO, CO<sub>2</sub>, NO<sub>2</sub>, etc.) not only helps the precursor material to disintegrate but also to dissipate the heat of decomposition, thus inhibiting sintering of the fine particles during the process.

Over fifty different ceramic oxides have been synthesized by the authors using the developed processes and the resulting powders are nanosized (10 to 90 nm in diameter), narrow particle size distribution of high purity and are obtained at relative lower pyrolysis temperatures than those reported in literature so far. The methods are versatile and can be extended for the preparation of a variety of mixed-oxide systems. In addition, the methods are technically simple, and time and energy efficient, which makes the process cost effective and commercial viable for large-scale production of the fine mixed-oxide products.

#### **O-2-177: New Improvements of TRXRD Experiments at Lure on H10 Beamline**

*D. Vrel<sup>1,7</sup>, S. Paris<sup>2</sup>, N. Girodon-Boulandet<sup>1</sup>, J.-F. Mazué<sup>2</sup>, E. Couqueberg<sup>2</sup>, M. Gailhanou<sup>3</sup>, D. Thiaudière<sup>3,4</sup>, E. Gaffet<sup>5,7</sup>, F. Bernard<sup>2,7</sup>, J.-C. Gachon<sup>6,7</sup>*

*<sup>1</sup>LIMHP, UPR 1311 CNRS, 99 avenue J.-B. Clément, 93430 Villeurbanne, France*

*<sup>2</sup>LRRS, UMR 5613 CNRS/Université de Bourgogne, BP 47870, 21078 Dijon Cedex, France*

*<sup>3</sup>LURE, UMR 130 CNRS/CEA/MENRT, Bat 209D, Université Paris Sud, 91405 Orsay Cedex, France*

*<sup>4</sup>CRMHT, UPR 4212 CNRS, 45071 Orléans Cedex 2, France*

*<sup>5</sup>UMR 5060 CNRS, "Far from Equilibrium Phase Transitions" group, 90010 Belfort Cedex, France*

*<sup>6</sup>LCSM, UMR 7555 CNRS/Université Nancy I, BP 239, 54506 Vandœuvre-lès-Nancy Cedex, France*

*<sup>7</sup>GFA, GDR 2391 CNRS, J.-C. Nipce, LRRS, 9 av. A. Savary, BP 47870, 21078 Dijon Cedex, France*

In order to control SHS reactions, a better understanding of the initial conditions is usually sought, as the initial conditions are the easiest, if not the only parameters we can use to control the reaction. Many different characterizations have been used for this purpose, as well as to determine the properties of the products. More and more, however, this approach appears to be insufficient, and the characterization of the chemical and physical path *during* the reaction through in-situ measurements is necessary. Aside from thermocouples and thermography, which can provide a reliable measure of the *thermal* history of the reacting sample, tools providing information about the *chemical* path such as QEXAFS or Time-Resolved XRD become increasingly important in our understanding of SHS reactions.

From the 1999 experiments, the TRXRD experiment has been transferred from the D43 to the H10 Lure beamline, and we took the opportunity to do more than adapt the existing experiment. As a result, here are the experiment improvements:

- The H10 beamline optics provides horizontal and vertical focusing of the beam coming out of a bending magnet. As a result, a 3 mm x 500µm spot can be obtained with no flux loss, much brighter than D43.

- The sample holder has been completely redesigned, to allow a fast sample setup, easily adjustable distance between igniter and sample, and energy within the igniter. This holder has been designed for the 4+2 circles goniometer available on H10 beamline, also featuring a translational adjustment, allowing us to chose the analyzed point at the sample surface.
- The chamber coming on top of this holder is of limited volume, thus providing a high and fast purity of the He atmosphere. Beside a 190° Kapton window for X Ray analysis, two fluorine windows have been added, thus providing a good transparency from near UV to mid-IR spectrum. One of this window is very large, allowing a very short working distance with the IR camera, and thus a good spatial resolution.
- The 190° Kapton window being exclusively used for X Rays, we have been able to use an Inel CPS 120 curved detector, with a maximal 2θ range of 120°. For practical reasons (especially peak definition) we chose to use a 80° 2θ range.
- This detector is connected to two different electronics, one fast but limited in channel and time, the other much slower but with greater data storage. We are now therefore able to analyze on the same experiment the fast part of the reaction together with post-combustion, recrystallization, or other phenomena with longer time scales.
- Finally, small home-made softwares have been designed to check the result of a given experiment immediately.

We will present all these different new exciting features in more detail by the use of some examples from our latest experiments in December 2000.

### **O-1-19: Novel Evolutionary Modeling of SHS Systems**

S.E. Zakiev

*ISMAN, RAS, Chernogolovka, 142432 Russia*

The successful examination of many SHS-problems, such as actions by external fields of the different physical nature, requires development of new methods of modeling. There is necessity in dynamics detailing of considered processes in quite small time and space scales. The building-up of such procedures can not be rested on a known local quasi homogenization principle of SHS-system. As the experiments testify [1], the passage to small scales carries on not to homogenization of the system medium, but on the contrary, to its dividing into some components. For example into two parts: on structure composed from actively react surface layers of SHS granules, which exists during period of time smaller then  $10^{-2}$  c, and on a chemically inactive part of a system. Thus appears a quite important modeling problem. Indicated parts spatially are disproportionate one another. So, for example, total volume of above-stated reactive structure is vanishingly small on matching not only with total volume of a system, but also with total volume of a reactionary zone.

The modern statistical different heterogeneous systems examinations have established for many actual objects a possibility of spatially vanishingly small components mathematical interpretation as structures having fractional dimensionality. The one-dimensional mathematical method of heterogeneous system modeling, which based on such interpretation, is compounds essence of this work. The application of a procedure is illustrated by an example.

1. A. S. Mukasyan, A. S. Rogachev, A. Varma. Mechanism of reaction wave propagation during combustion synthesis of advanced materials. Chemical Engineering Science 1999, vol. 54, pp. 3357-3367.

This work is supported by Russian Foundation for Basic Research, grant RFBR 01-03-32683a.

### **O-3-89: On Combustion Behavior of Nano-Scale SHS Reactions**

*Chien-Chong Chen, Ming-Chien Chiu*

*Chaoramics Laboratory, Department of Chemical Engineering, National Chung Cheng University*

*Chia-Yi 621, Taiwan*

The influences of nanoparticles on combustion behavior were investigated by nano-scale SHS reactions between powders of titanium (-100 mesh or -325 mesh) and carbon, which contained x wt. % of nano carbon ( $\sim 4$  nm) and (100-x) wt. % of graphite (-325 mesh). To prepare reactant pellets with the same density, the imposed compaction pressure was proportional to the content of nano carbon. As the content of nano carbon increased, both the combustion velocity and temperature were raised initially in a linear fashion and followed by a slightly exponential trend. The variation from the linear to the nonlinear dependence of combustion velocity and temperature on the content of nano carbon was more significant for the smaller Ti particles. Comparing the reactant pellets prepared by the dry and wet mixing methods, combustion velocity of the latter was larger, indicating wet mixing could better disperse the nano powders. Another finding was that the combustion mode transformed from the steady to unsteady combustion, when content of nano powder increased. Moreover, the ignitability of reactant pellet was dramatically enhanced. When carbon was of 100% nano carbon, reactant pellets could be easily ignited by a 150 W of electrical energy, or even could be ignited by a cigarette lighter!

### **O-1-25: On Combustion Wave Structure at SHS of Composite Ceramics of BN-SiO<sub>2</sub>**

*V.E. Loryan, I.P. Borovinskaya*

*Institute of Structural Macrokinetics and Materials Science, RAS*

*Chernogolovka, Moscow Region, 142432, Russia*

Combustion of a mixture of boron + silicon dioxide (up to 70%) in nitrogen was investigated at nitrogen pressure of 70-100 MPa. In this case the burning rate was equal to 6.0-8.0 mm/s, the combustion temperature ranged from 2250 to 2500°C.

The residual porosity after the fast reaction zone propagation is shown to be a regulator of the processes occurring in the zones following the combustion wave.

The distribution order of the chemical-physical processes, namely:

- densification of the samples due to the reaction volume effect, shrinkage, and gasostatic pressing;
- melting, crystallization, and amorphization of initial components and combustion products;
- partial interaction of boron and nitrogen;
- after-nitriding of the residual boron;
- solid-phase interaction of initial components;

by the combustion wave zones is described in the paper.

This work is supported by Russian Foundation for Basic Research, grant RFBR 00-15-99054.

### **O-2-28: On Theory of “Cold Ignition” of Combustion-Like Waves in Solid-Phase Reactions**

*Alain Pumir<sup>1</sup>, Viktor V. Barelko<sup>2</sup>*

*<sup>1</sup>Institut Non Linéaire de Nice <[pumir@inln.cnrs.fr](mailto:pumir@inln.cnrs.fr)>*

*1361, Route des Lucioles 06560 Valbonne, France*

*<sup>2</sup>Institute of Problems of Chemical Physics, R.A.S. <[barelko@icp.ac.ru](mailto:barelko@icp.ac.ru)>*

*Chernogolovka, Moscow Region, Russia*

Fronts of weakly exothermal chemical reaction may propagate in solids at very low temperatures (liquid nitrogen and helium temperatures) thanks to a quite unusual thermal mechanism, involving a feedback between the heat produced by the reaction and the disruption of the solid matrix. In this class of phenomena, the reaction may be induced by mechanical constraints, without a large elevation of temperature.

On the basis of a simple phenomenological model, we investigate ignition of a propagating front by initially (i) disrupting a localized zone of the solid matrix, or by (ii) introducing a temperature jump, leading to a thermal shock with strong temperature gradients. In particular, we show that reaction can be initiated by disrupting only a very small fraction of the sample under very weak heating ("cold ignition").

Application of the theory as a new approach to the problem of initiation of solid explosives by friction or shock is discussed.

### **O-2-23: Pollution-Free SHS Generator of Fire-Extinguishing Aerosol**

*A.P. Amosov, A.R. Samboruk, V.A. Rekshinsky, A.G. Makarenko,*

*E.V. Kuznets, Samara State Technical University*

*141 Galaktionovskaya Street, Samara, 443010, Russia*

*E-mail: [mvm@dp.sstu.samara.ru](mailto:mvm@dp.sstu.samara.ru)*

Conventional fire-extinguishing aerosol are finely divided toxic oxides and carbonates of alkaline metals suspended in gaseous nontoxic products of combustion: N<sub>2</sub> and CO<sub>2</sub>. These products contain also impurities of products of incomplete oxidation of combustibles: CO, NH<sub>3</sub> HCN, NO<sub>x</sub> and Cl<sub>2</sub> (pollutants), which exert toxic effect on personnel situated in a room protected by fire-extinguishing means on the base of such aerosols. At same time, HCN, NO<sub>x</sub>, and NH<sub>3</sub> are the ozone - destroying substances. The oxides of alkaline metals are easily hydrolyzed in the humid air, and alkalis formed impair equipment. In this case, operating and maintenance personnel must be removed from the room.

Our experience in research and development of SHS azide processes helped us to formulate new compositions on the base of azide of sodium or potassium as a combustible aerosol forming reagent. The use of perchlorate of sodium or potassium as an oxidizing agent, and chlorinated polyvinyl chloride resin as a binder with enhanced content of chlorine allows making the aerosol with the dispersed phase consisting of chlorides of sodium and potassium in N<sub>2</sub> and CO<sub>2</sub> as the result of the SHS-process. As this takes place, combustion products do not contain the highly toxic oxides of sodium and potassium as well as the lower oxides of nitrogen and carbon, and the cyanides. This improves the environmental safety of the gas-forming aerosol, reduces the harmful effect on the personnel in the room protected, and increases the fire-extinguishing ability.

An original structure of the SHS generator gives an increase in the rate of combustion and aerosol forming, and a decrease in the temperature of the aerosol generated, that improves characteristics of the generator.

These results are presented in application for a patent no. 2000126609 of 25<sup>th</sup> October 2000 in Russia Slate Patent Office.

### **O-2-39: Peculiarities of the Functionally Graded Targets Formation in Combustion Wave of the SHS-Systems with Working Layer Ti-Si-B, Ti-Si-C, Ti-B-N, Ti-Al-B, Ti-C**

*E.A. Levashov<sup>1</sup>, B.R. Senatulin<sup>1</sup>, H.E. Grigoryan<sup>1</sup>, A.S. Rogachev<sup>1</sup>, J.J. Moore<sup>2</sup>*

*<sup>1</sup>SHS-Center of the Moscow Steel and Alloys Institute (Technological University) and the Institute of Structural Macrokinetics and Material Science of RAS, Leninsky prospect, 4, 164, Moscow 119991, Russia , Phone: +(095) 230-4500, Fax: +(095) 236-5298*

*<sup>2</sup>Advance Coatings and Surface Engineering Laboratory, Colorado School of Mines Golden, Colorado, 80401-1887, USA*

Investigation results of bi- and ternary layers composite targets for reactive bias magnetron sputtering produced using force SHS-pressing technology were presented in the paper. Functionally Graded Materials (FGM) approach allowed a synthesis of heat- and wear resistant porousless materials with an operating layer on the base of TiB<sub>2</sub>, Ti<sub>5</sub>Si<sub>3</sub>, Si phases for Ti-Si-B, TiC, Ti<sub>3</sub>SiC<sub>2</sub>, TiSi<sub>2</sub> (SiC) - for Ti-Si-C system, TiB<sub>2</sub>, TiN - for Ti-B-N system, TiB<sub>2</sub>, TiAl - for Ti-Al-B system, and TiC<sub>0.5</sub> -for Ti-C system.

TiC-TiB<sub>2</sub>, TiB-Ti, TiC<sub>0.5</sub>, TiB<sub>2</sub>-Cu, and TiB<sub>2</sub>-TiN-Cu compositions were used as underlayers or intermediate layers.

Experimental exothermal mixture compositions were chosen by means varying coefficients "x" and "y" in chemical reactions equations: (100-y)(Ti+2B)+ySi,

$x(Ti+2B)+(100-x)(5Ti+3Si)$ ,  $3Ti+ySi+2C$ ,  $(100-x)(Ti+C)+x(5Ti+3Si)$ ,  $(100-y)(Ti+2B)+yAl$ ,  $x(Ti+2B)+(100-x)(Ti+Al)$ . Macrokinetic parameters of combustion processes, and also regularities of phase- and structure formation of the synthesis products were studied.

Strong coalescence between the layers is achieved owing to an evident transitional zone 1-2 mm in the thickness, the zone being a consequence of a high combustion temperature and its existence in the combustion wave in the boundary separating the layers of a significant amount of the combustion products and semi-products melts. The melts impregnate the porous body formed by high refractory compositions.

Concentration profiles of Ti, Si, C, Cu distributions are taken in the cross-section of functionally graded targets. Fracture microstructures and hardness distributions through the target thickness were studied in the work.

The SHS-targets were successfully used in PVD technologies for the synthesis of multifunctional thin films and ultrahard coatings in particular.

#### **O-3-41: Physical Chemical and Technological Aspects for Application of Novel SHS-Refractory Ceramic Materials**

*M.R. Filonov<sup>1</sup>, E.A. Levashov<sup>1</sup>, I.P. Borovinskaya<sup>2</sup>, V.A. Bunin<sup>2</sup>,  
A.V. Korshikov<sup>1</sup>*

*<sup>1</sup>SHS-Center of the Moscow Steel and Alloys Institute (Technological University) and the Institute of Structural Macrokinetics and Material Science of RAS, Leninsky prospect, 4, 164, Moscow 119991, Russia, , Phone: +(095) 230-4500, Fax: +(095) 236-5298*

*<sup>2</sup>The Institute of Structural Macrokinetics and Material Science of RAS, Moscow region, 142432, Chernogolovka, Russia*

Application of SHS refractory materials is a very advance for the metallurgical industry. Composition and properties of ceramic materials on base of BN, TiB<sub>2</sub>, SiAlON, AlN and Si<sub>3</sub>N<sub>4</sub> produced by the method of filtration combustion were studied. A series of investigations for measuring refractoriness, thermoresistance, mechanical strength, resistance to metallurgical melt at the temperature 1500-1700°C, and thermogravimetric and dilatometric researches were carried out. Refractoriness degree was determined according to change of geometric dimensions, weight and phase state after heating to 1600, 1800 and 2000°C.

A low wetting degree of refractory materials by melts on the base of Fe, Ni and Co and absence of their chemical interaction are very promise characteristics of SHS ceramics. Investigations of interactions between SHS compositions and metallurgical slag were carried out to estimate their resistance in ion solutions. It was established that the properties of SHS-ceramic materials strongly depend on the amount of unreacted initial elements in final product, and collateral substances, which arise during the high-temperature synthesis.

The most promising compounds characterized by low wear-resistance properties are compositions on the base of BN. Because of low level of mechanical properties, it is necessary to use BN with additions of other refractory materials such as Al<sub>2</sub>O<sub>3</sub>, CaO, TiB<sub>2</sub>, SiC, etc. Refractory SHS-ceramic materials for various purposes were tested in the metallurgical plants of Russia. Laboratory and industrial crucibles for melting metals and alloys, refractory products for pouring, conduits for liquid metal, sliding shutters, thermocouple covers, etc. were fabricated. It has been shown that these materials much more exceed conventional oxide ceramics, which used at the present time.

The effect of SHS-ceramic powders additions into conventional oxide ceramics was investigated in two directions: the addition to oxide matrix and creation the protective layer on the surface of oxide articles. It was established the BN-TiB<sub>2</sub>, BN-Al<sub>2</sub>O<sub>3</sub> compositions can be recommended as the most promising refractory materials for the metallurgical industry.

This work is supported by Russian Foundation for Basic Research, grant RFBR 00-15-99054.

#### **O-3-74: Pressure-Assisted Reactive Processing of Mg-SiO<sub>2</sub> Powder Blends**

*I. Gutman<sup>1</sup>, L. Klinger<sup>1</sup>, I. Gotman<sup>1</sup>, M. Shapiro<sup>2</sup>*

<sup>1</sup>*Faculty of Materials Engineering, Technion, Haifa 32000, Israel*

<sup>2</sup>*Laboratory of Transport Processes in Porous Materials Faculty of Mechanical*

*Engineering, Technion, Haifa 32000, Israel*

SiO<sub>2</sub> is one of the most common materials in nature and it exists in both crystalline and in amorphous forms. High reactivity between Mg and SiO<sub>2</sub> can be utilized for Self-propagating High-temperature synthesis (SHS) of attractive structural materials. Reaction between Mg and SiO<sub>2</sub> can produce a limited amount of products: pure silicon, oxide ceramics (different phases of magnesium silicates and MgO) and Mg<sub>2</sub>Si silicide.

Mg-SiO<sub>2</sub> blends of different stoichiometry were used for the experiments. Two reactive processing methods have been chosen, thermal explosion (TE) under pressure and reactive hot pressing (RHP). The materials obtained were characterized by X-ray diffraction (XRD) and SEM with quantitative chemical analysis (EDS).

Under the TE regime the reaction products were mainly Periclase-MgO, Forsterite-Mg<sub>2</sub>SiO<sub>4</sub>, Mg<sub>2</sub>Si and Si. The reaction was initiated at temperatures as low as 200-400°C. To obtain denser SHS products TE under pressure was successfully used.

In order to study the kinetics of the reaction at different temperatures, a model system consisting of SiO<sub>2</sub> bulk immersed into Mg powder was employed. The "diffusion couple" assembly was annealed in a 500-640°C temperature range. The reaction zone formed had an unusual structure consisting of thin periodically spaced MgO and Mg<sub>2</sub>Si layers parallel to the SiO<sub>2</sub> surface. The rapid reaction zone growth obeyed the parabolic law typical of diffusion controlled processes, and was characterized by a very low activation energy.

The periodic structure of the reaction zone and its rapid growth suggest that fine-scale interpenetrating phase composites can be formed in the process of RHP at low temperatures and/or over short periods of time. The influence of powder size and SiO<sub>2</sub> crystallinity/amorphousness on SHS and solid state reaction kinetics and on products morphology has been studied.

#### **O-2-110: Functionally Gradient Materials in the Al<sub>2</sub>O<sub>3</sub>–SiC–Ti<sub>3</sub>SiC<sub>2</sub> System and Their**

##### **Characteristics**

*M. Lopacinski, J. Lis*

*Department of Advanced Ceramics*

*Faculty of Materials Engineering and Ceramics*

*Academy of Mining and Metallurgy, Cracow, Poland*

In this work the authors present preliminary results of research on preparation and characteristics of ceramic Functionally Gradient Materials (FGMs) with increased impact resistance in the Al<sub>2</sub>O<sub>3</sub>–SiC–Ti<sub>3</sub>SiC<sub>2</sub> system. Titanium silicon carbide Ti<sub>3</sub>SiC<sub>2</sub> and silicon carbide SiC powders have been synthesised using the method of Self-propagating High-temperature Synthesis. Subsequently, homogeneous mixtures of Ti<sub>3</sub>SiC<sub>2</sub>, SiC and Al<sub>2</sub>O<sub>3</sub> powders in various compositions have been prepared. These mixtures were then used as layers in the multi-layer Functionally Gradient Materials. After thermal processing in a hot-press the materials were tested. Chemical and phase composition of individual layers, hardness and hardness distribution across the composite thickness and impact resistance of the gradient beams were investigated. It was found that these materials could be applied as elements of ceramic armour materials.

## **O-1-18: Generation of Reaction Spots in a Gasless Combustion Front under the Influence of Heat Losses**

*B.L. Kopeliovich*

*A.V. Luikov Heat and Mass Transfer Institute of the National Academy of Sciences of Belarus, 220072 Minsk*

Numerical study of gasless combustion of a mixture, enclosed in a narrow cylindrical channel, shows that heat wave undergoes the cyclic changes under the conditions of intense heat removal. The reaction retardation wave appears periodically on the surface of the combustion front, suppresses the activity of chemical sources and carries the influence of heat losses up to the deep layers of mixture. The retardation wave is enhanced on reflection from the axis. When this wave meets an obstacle in the form of a front deflection near the envelope, that becomes steeper and increases the chemical reaction rate  $W_{fr}$  ahead of itself. The retardation wave slows down in a radial direction and acquires the rotational impulse according to the impulse conservation law. The region of high values of  $W_{fr}$  contracts gradually and turns into a reaction spot at the moment when weak discontinuity appears in tangential velocity of front propagation. Reaction spot movement on the front surface is accompanied by the displacement of a thermal spot in the region of products. Thus, the term 'hot spot' which does not distinguish these conceptions is not quite correct. The solution of the conjugated problem of heat conduction with an axial symmetry is valid for all the radial sections and results in periodical birth of reaction spots that merge into a rotating ring. A hypothesis is advanced concerning the nature of multi-point and spin combustion.

**Key words:** heat wave, reaction retardation wave, reaction spot, thermal spot.

## **O-2-120: Pressure-Assisted SHS of $Ti_2AlC$ and $Ti_3Al_{1.1}C_{1.8}$**

*Y. Khoptiar, I. Gotman, E.Y. Gutmanas*

*Faculty of Materials Engineering, Technion, Haifa 32000, Israel*

The ternary compounds  $Ti_2AlC$  and  $Ti_3Al_{1.1}C_{1.8}$  exhibit a layered graphite-like crystal structure and are known as "Machinable Ceramics". They possess high thermal shock resistance, high oxidation resistance, good machinability and electrical and thermal conductivities comparable to those of pure metals. In the present work,  $Ti_2AlC$  and  $Ti_3Al_{1.1}C_{1.8}$  were synthesized from elementary powder blends employing the Thermal Explosion (TE) mode of Self-propagating High-temperature Synthesis. To overcome the porosity inherent in SHS products Thermal Explosion under Pressure was employed. This technique has an advantage of the lower furnace temperatures and considerably shorter processing times compared to the related Reactive Hot Pressing method (RHP).

The obtained products were characterized using XRD, SEM and EDS techniques. *In situ* temperature measurements in the samples during the synthesis were performed. Modeling of the synthesis was based on the analysis of the obtained temperature curves coupled with specimen characterization results.

For both compounds SHS synthesis occurred in two stages: 1) formation of Ti-aluminides and 2) reaction of the aluminides with graphite to form the final product. Certain thermo-physical conditions were required to initiate the second stage reaction. In the case of  $Ti_3Al_{1.1}C_{1.8}$  the second stage went through formation of intermediate  $Ti_2AlC$  and  $Ti_3AlC$  compounds. The final product in both cases had a laminate structure with a relatively fine grain size ( $\leq 10 \mu m$ ) and contained small fractions of TiC and Ti-aluminides. The effect of the initial blend composition and powder size on the phase composition, microstructure and porosity of the product was studied. The application of uniaxial moderate pressure during TE synthesis (Reactive Forging) allowed the production of near fully dense samples.

## O-1-181: Qualitative Analysis of Physical and Physicochemical Effects Leading to the Intrinsic Electrical Voltages in SHS-Waves Propagation Fronts

I.A. Filimonov<sup>1</sup>, N.I. Kidin<sup>2</sup>

<sup>1</sup>*Institute of Structural Macrokinetics and Materials Science Russian Academy of Sciences*

*Chernogolovka, Moscow Region, 142432 Russia*

<sup>2</sup>*Institute for Problems in Mechanics Russian Academy of Sciences*  
*101, bld. 1, prosp. Vernadskogo, Moscow, 117526 Russia*

Different physical and physicochemical effects that could lead to the electrical voltage difference during SHS-wave propagation are under consideration. Namely, they are thermoelectric power, electrostriction, and contact voltage difference at the interface of metals with different physical features. Voltages arising due to electrochemical effects similar to electrolytic bath are under discussion, as well as nonohmic semiconductors conductivity, contacts of dielectrics with other materials and other effects arising due to gradient of electric conductivity.

Results are compared with experimental data available from the literature.

## O-3-174: Reactivity Study of a Dense Nanostructured MoSi<sub>2</sub> Elaborated from MAFAPA Process

Ch. Gras<sup>1,2</sup>, E. Gaffet<sup>2</sup>, JP. Larpin<sup>1</sup>, C. Valot<sup>1</sup>, Z.A. Munir, F. Bernard<sup>3</sup>

<sup>1</sup>*LRRS, UMR5613 CNRS – Université de Bourgogne, BP 47870 21078 Dijon, France*

<sup>2</sup>*Far from Equilibrium Transitions Phases Group, CNRS UMR, 5060 - 90010 Belfort, France*

<sup>3</sup>*Department of Chemical Engineering and Materials Science, University of California, Davis CA 95616, USA*

A new process combining an electric field activation and an imposition of pressure starting from mechanically activated powder mixtures is demonstrated as a means to simultaneously synthesize and densify nano-MoSi<sub>2</sub> in one step. Mo + 2Si powders were co-milled in a specially designed planetary mill to obtain nanometric reactants but to avoid formation of any product phases [1]. These were then subjected to high AC currents (1.6 kA) and pressure of 106 MPa. Under these conditions, a reaction is initiated and completed within a short period of time (3-6 min). The process is demonstrated in this work by the synthesis of dense nanostructured MoSi<sub>2</sub>. The crystallite size has been found to be about 68 nm. In addition, the relative density of the end-product ranged from 82 to 93 %.

Consequently, it was possible to compare the behaviors of these end-products to those of the products which have been prepared using the same procedure but without a mechanical activation step. Two properties in this work were investigated: the hardness and the high temperature resistance. Firstly, it seems that the hardness of MoSi<sub>2</sub> elaborated from the MA step (1500 HV) is greater than the hardness of MoSi<sub>2</sub> prepared without MA step (1000Hv). Secondly, from an isothermal oxidation at 1273K during 24 h, only the products made from MA powders develop a protective layer (the thickness ranged from 40 nm) of SiO<sub>2</sub>. The improvement of the hardness and the high temperature resistance were respectively investigated.

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## **O-2-107: The Role of Liquid- and Gas-Phase Constituents of the Organic SHS Mechanism in Formation of Piperazine Malonate Microstructure**

*E.G. Klimchuk, V.I. Ponomarev, A.G. Merzhanov*

*Institute of Structural Macrokinetics and Materials Science of RAS*

*Chernogolovka, Moscow Region, 142432 Russia*

One of the major scientific problems in the field of SHS is establishment of relation: «synthesis conditions» - «interaction's mechanism» - «product's structure». For its decision the microstructure of solid-phase products, formed in different conditions, is studied. On the other hand, investigation of organic solids structure is an independent actual research task.

The piperazine-malic acid system is first and most simple studied system, on the base of which the model conceptions about organic SHS are being formed. The preliminary researches of the process of formation of solid organic salt - piperazine malonate - had shown that the basic mechanism of interaction in the SHS wave was the melting of low-melting piperazine and its capillary spreading in a three-dimensional matrix made by crystals of malic acid.

Methods of optical and electronic microscopy, DTA, dynamic X-ray analysis, quantum chemistry, video recording were used for the investigation. Crystalline piperazine malonate was synthesized in various conditions (temperature, type of reagents transport, phase condition etc.).

It was found out that melting of piperazine particles occur just in a points of contact at reagents mixing at room temperature, with formation of final product fine crystals consolidated afterwards. Formation of trace amounts of product crystals was watched simultaneously in a gas phase. Subsequent slow interaction at room temperature proceeded mainly by the sublimation of volatile piperazine and its surface reaction with malic acid crystals. These processes were accompanied by formation of characteristic surface microstructures - globules, clusters, etc.

The microstructure of an initial mix was decomposed at SHS. That was caused by fully melting of piperazine. The product of SHS consisted of edged micro crystals having wide function of distribution on the sizes. The average size of micro crystals (5  $\mu\text{m}$ ) was much lower than those of initial reagent crystals ( $\sim 100 \mu\text{m}$ ). That is a consequence of the bad solubility of a product in a melted piperazine. Separate big crystals grown, probably, from nucleus formed already at preparation of an initial mix, were observed. The presence of small quantity of needle crystals and through pores indicated that insignificant interaction in a gas phase occurred.

The possibility of molecules to react in a gas phase and on a surface of crystals was confirmed by quantum-chemical calculations. Kinetic date are in good agreement with microstructures dynamics observed. The role of liquid- and gas-phase processes in formation of piperazine malonate structure is discussed.

## **O-2-20: Self-Propagating High-Temperature Synthesis and Solid-State Reactions in Thin Films**

*V.G. Miagkov, L.E. Bykova*

*L.V. Kirensky Institute of Physics SB RAS, Krasnoyarsk, Russia*

Self-propagating the high-temperature synthesis (SHS) on powders has been widely studied, however, the study of SHS on bilayer film systems has just begun. If reagents are in form thin films sputtered successively one onto another, SHS occurs between them when the temperature of sample exceeds the temperature of initiation. The distribution SHS front is easy to observe visually. Self-propagating the nature of distribution SHS front is determined by reaction zone coinciding with the interface of the initial film and reaction products. Intensive heat output on the front exceeds the temperature on the front considerably. As a result Arrhenius diffusion dependence on temperature, the burning process proceeds exclusively on the front. The proposed SHS mechanism in thin films is analogous to process explosive crystallization. It is justified that SHS determines various solid-state reactions in thin films and multilayers. SHS occur also at depositing one layer onto other, if the temperature of the substrate exceeds the temperature of initiation. SHS in thin

films proceeds at low temperatures and number reagents, for which the synthesis is possible, is bigger than in SHS powders. The finding of temperature of initiation and phases generated in product of reactions are important one for the technical applications. SHS in thin films has both properties with in SHS powders and important differences. The most unexpected difference is the existence multiple SHS (MSHS) in thin films. MSHS in contrast to SHS represents convertible structural phase transition and corresponds transition through temperature of eutectics of bulky samples. However, in thin films MSHS occurs in solid-state phase (!) and there is phase decomposition as at eutectic solidification of bulky samples. The formation of reaction products of occurs at temperature of MSHS initiation. The review of literature shows that many solid-state phase transitions occurring in autowave regime in solid-state phase (explosive crystallization, solid-state polymerization, metal-insulator phase transition in vanadium dioxide  $VO_2$ ) are quite similar to SHS and MSHS in thin films and supposes common chemical mechanism of these phenomena. This supposes that the temperature of the SHS and MSHS initiations may coincide with the temperature of solid-state phase transitions in reaction products. It has been shown indeed that the temperature of metal-insulator phase transitions in  $FeS$  coincides with the temperature of SHS initiation in  $Fe/S$  bilayer film system. The connection between the SHS phenomena and order-disorder phase transition has also been found for the classical system  $Cu-Au$  in the theory of ordering. It has been shown that the temperature of SHS initiation in  $Cu/Au$  bilayer film system coincides with the temperature of the ordering  $CuAu$  superlattice. This can also be observed in the other film systems whose products of reaction result in superstructures.

#### **O-2-12: Self-Propagating High-Temperature Synthesis of Polymers of Acrylamide**

##### **Complexes of Transient Metals**

A.G. Merzhanov, A.M. Stolin, L.S. Stelmakh

*Institute of Structural Macrokinetics and Materials Science,*

***RAS, CHERNOGOLOVKA, 142432 RUSSIA***

Rather perspective usage of the approaches both methods of the SHS theory and practice and frontal polymerisation in new processes self-propagating high-temperature synthesis of polymers is represented, in which one initial components and the finished products are solid. The power effects give a unique capability to mould off-the shelf items from composite metalpolymers.

In the present activity some outcomes on research of the makrokinetic characteristics of SHS of polymers ( wave propagation velocity of reacting, maximum temperature of reaction and their dependencies on the initial density of a sample) are represented, which one demonstrate a capability of this process realisation. As the object of the investigation the finely divided powdery monomer of acrylamide with the components of different nitrates salts of transient metals was selected.

The analysis of process with the help of a photo and videoshooting of a reaction mixture of powders, and also with the help of calorimetric methods is conducted. A distinctive feature of auto wave process for systems of organic acrylamide powders with metalopolymers is originating a fluid phase during synthesising, and bound with it effects of capillary dipping. The liquid zone is appreciable visually and its characteristic sizes can amount some millimetres. Besides, the crystallisation front in reaction products is allocated. Thus, the process investigated is characterised by the presence of three fronts: 1- separates initial components from a polymer melt, 2- separates a fluid phase from the solid product, 3- the crystallisation front. The behaviour of different interdependent processes of a crystallisation and polymerisation, the different phase condition of a material cause particular features of SHS of polymers.

Is established, that maximum temperature grows with increase of density, and the front propagation velocity drops. This abnormal outcome is absolutely not typical for processes of classic thermal self-propagation. It is possible to explain this result by a gravitational filtration of a fluid phase in pores and intensive mixing of a melt escaping gases at polymerisation, a thermal diffusivity of a system as a result of which is effectively increased. At increase of material density the thermal

diffusivity is reduced and as a result the speed drops. Thus, macrokinetics regularity of SHS of polymers can have different anomalies, which one are required detail arguing and research.

### **O-1-9: SHS Fabrication of Alumina-Reinforced High-Temperature Alloys**

*N. Travitzky<sup>1</sup>, N. Claussen<sup>1</sup>, E.Y. Gutmanas<sup>2</sup>*

*<sup>1</sup>Advanced Ceramics Group, Technische Universität Hamburg-Harburg, Germany*

*<sup>2</sup>Technion, Haifa, Israel*

Super alloy-type materials are used in a variety of high temperature applications, e.g. in aircraft and energy industry. Reinforcement of such alloys with alumina can lead to enhanced creep and flexure strength. A variety of SHS techniques have been developed lately with potential for low-cost and rapid manufacturing of advanced composites. The in situ infiltration (isi) process is presently being studied both at Technion and TUHH to fabricate alumina-reinforced heat-resistant alloys. These composites termed isi-3A and isi-MMC are fabricated by subjecting a powder compact, containing Al and reactive oxides along with additional constituents of a given heat resistant alloy to mild pressures and modest temperature so as to cause a termite-type reaction. Dense, alumina reinforced Fe- and Ni-based alloys were fabricated by compacting powder mixtures (e.g.,  $\text{Fe}_2\text{O}_3$ , Fe, Ni, Cr, Al for Fe-based alloys and  $\text{Cr}_2\text{O}_3$ , CoO, Ni, and Al for Ni-based composites) at 900°C and 20 MPa for less than 5 min. The composites prepared exhibit novel microstructures along with high bend strength and toughness. Processing details, microstructure, and mechanical properties of the as-fabricated composites will be presented.

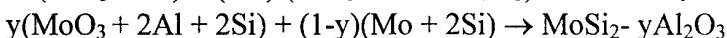
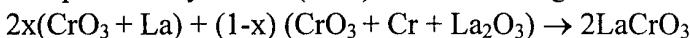
### **O-2-6: SHS of Oxide and Composite Materials under Centrifugal Forces**

*V.I. Yukhvid<sup>1</sup>, V. N. Sanin<sup>1</sup>, M. D. Nersesyan<sup>1,2</sup>, D. Luss<sup>2</sup>*

*<sup>1</sup>Institute of Structural Macrokinetics and Materials Science, Chernogolovka, 142432, Russia.*

*<sup>2</sup>University of Houston, Houston, TX 77204-4792, USA*

$\text{LaCrO}_3$  oxide and  $\text{MoSi}_2\text{-Al}_2\text{O}_3$  composite material were produced by Self-Propagating High-Temperature Synthesis (SHS) under centrifugal forces by the following exothermic reactions:



The combustion temperatures of either reaction was very high and generated a molten product when x (y) exceeded 0.5 (0.7). Experiments were conducted in both radial and axial centrifuges at 1-1000 g under atmospheric pressure. We studied the impact of the centrifugal overload (and its vector direction) on the combustion parameters, reaction mechanism, combustion front propagating mode, product (including tubular) phase and chemical composition, microstructure and other properties.

### **O-4-67: SHS Regularities and Properties of TiC – SiC Composite Powder and Compact Material**

*S.S. Mamyany, D.Yu. Belov, A.A. Boldin*

*Institute of Structural Macrokinetics and Materials Science, Chernogolovka, Moscow Region, 142432, Russia*

Our work is dedicated to obtaining composite material of TiC – SiC with various component content by the SHS method.

Titanium, carbon black, silicon, silicon carbide and titanium dioxide powders were used as the initial components.

In the system of Ti – C – Si we obtained powders containing up to 70 wt. % of SiC. In the system of Ti – C – SiC we obtained powders containing up to 35 wt. % of SiC.

Influence of a component ratio, partial replacement of initial elements by their oxides (Ti by  $\text{TiO}_2$ ), initial mixture density, and inert gas pressure on burning rate, product phase and chemical composition, material structure and properties was studied.

Materials in the system of TiC – SiC were obtained by the methods of sintering and SHS densification. Physico-mechanical properties of the materials obtained by these ways are compared in the paper.

This work is supported by Russian Foundation for Basic Research, grant RFBR 00-15-99054.

#### **O-1-135: SHS Synthesis of Titanium Silicides and Their Properties**

*M. Lopacinski, J. Lis, M. Cyganik, L. Chlubny,*

*Department of Advanced Ceramics, Faculty of Materials Engineering and Ceramics,  
Academy of Mining and Metallurgy, Cracow, Poland*

Silicides, e.g.: titanium silicides, are compounds of the  $T_2$ - $B_2$  type which have interesting electrical properties while retaining mechanical strength and corrosion resistance at elevated temperatures. However, except for molybdenum disilicide used as resistance heating elements, materials of this type have not found important applications yet and their properties are not known in detail. It has been thought that titanium silicide materials of optimum properties could be produced by using SHS because the specific conditions of this method permit an efficient production of compounds with bonds of a pronounced covalent character, what is the case with titanium silicides.

The paper describes the SHS of  $Ti_5Si_3$ ,  $TiSi_2$  and  $TiSi$  sinterable powders and microstructure and properties of dense materials produced from these powders by hot pressing. Determined were several mechanical characteristics and electrical resistivity at different temperatures. While  $TiSi$  shows electrical behavior typical of metallic conductors,  $TiSi_2$  is a semiconductor while  $Ti_5Si_3$  is a semiconductor below 140°C and a metallic conductor above this temperature. The latter two materials show typical properties of thermistors.

#### **O-4-141: SHS Technology an Industrial Reality**

*J. Artieda, S. Carretero, N. Makhonin, D.H. Hilera*

*SHS Ceramicas, 28040 Madrid Spain*

Since a long time ago the SHS technology has been a revolutionary technology up to date only apply in research centers, and without any industrial application.

SHS CERAMICAS, S.A. is the first industrial development for the use of the SHS technology.

The company has been founded by Spanish company ENUSA INDUSTRIAS AVANZADAS S.A. the Russian institute ISMAN. 70% of the company is owned by the Spanish company and the balance by the Russian part.

Located in the West part of Spain and near the Portuguese border, this fully new factory has been conceived with the highest functionality and computerization criteria. Reaching this target has been possible thanks to the very well reputed engineering department of ENUSA.

The production was started on summer 2000 with the silicon nitride. The product obtained was according to the specifications previously stated. On February of 2001 the production of the boron nitride has been started up. As in the silicon nitride case, the result was according to the specifications. Difficulties and results will be exposed during this session. Besides the silicon nitride and the boron nitride, SHS CERAMICAS, S.A. is carefully watching the advanced ceramic market in order to expands its commercial activities to other products. Despite the difficulties to enter in the advanced ceramic business we are very confident on our technology and our capabilities to make of SHS a profitable technology.

#### **O-2-128: Some Features for Increasing Stability of Single Crystal Growth at Plasma-Arc**

##### **Melting of SHS Products and Reactive SHS Mixtures**

*Yu.A. Sapronov, M.A. Ponomarev*

*ISMAN, RAS, Chernogolovka, Moscow Region, 142432 Russia*

In this work we investigated increase in the stability of single crystal growth at plasma-arc melting. We studied possibility of applying a special arc power modulating system for growth stabilization.

We investigated some growth features in case of application of rods and granules from the chemically active SHS compositions (for the Ti+C system taken as an example) as raw materials. The effect of melt feeding by starting material on the crystallization system stability at plasma-arc melting was examined. The stage of feeding with both rod and powder SHS raw material was found to cause plasma arc electrical characteristics oscillations, plasma flow asymmetry, melt temperature change, and melt fast crystallization. Such disturbances are often the main reason for the process destabilization.

The system of plasma arc power low-frequency modulation under specific conditions is the effective method for increase in crystal growth stability. The modulation system allows us to melt the solid phase layer has grown with a high rate in the ingot by the moment of feeding, and then to perform crystallization of a new layer with the desired (low) rate. Thus the influence of disturbances in the crystallization system on crystal growth is reduced. The most stable growth was shown to occur when the feeding is performed in the beginning of the stage of arc power modulated value increase. The regimes for arc power modulation were determined, such regimes ensure maximum reduction of disturbing influences on the melt during the feeding portions supply into the melting zone.

Application of rods and granules from the chemically active SHS mixtures contributed to a decrease in disturbance level at the feeding stage. Introduction of each portion into the melt is accompanied by chemical reaction in the initial material with the additional heat release. Due to this, the time of the active granules retention in the solid state on the melt surface was 3-4 times lower, than that of inert particles. Additionally, an increase in arc voltage and power occurred upon the introduction of chemically active granules melt into the bath because of the anode spot electrical characteristics change. Release of chemical energy from the active granules and simultaneous increase in the arc power were the factors decreasing the time and amplitude of action disturbing the melt during feeding. The melting rate of the chemically active feeding rod was 4 times higher than that of the inert rod. Thus, under specific conditions, application of reactive SHS mixtures as raw material leads to significant reduction in the thermal oscillations in the system and increases the growth stability.

### **O-3-5: Structural and Physicochemical Aspects of Iron by Chromium Substitution and the Effect of Magnetic Field in SHS-Produced Ferrites**

*Maxim V. Kuznetsov*

*Institute of Structural MacrokINETics and Materials Science, Russian Academy of Sciences,  
Chernogolovka, Moscow region, 142432 Russia*

Iron by chromium substitution and permanent magnetic field influence in all the types of ferrite materials: spinels, M-type hexaferrites, garnets, orthoferrites, solid solutions of iron oxides and chromium (III) oxide were discussed. Different aspects of chromium doping and magnetic field (up to 1.1T) influence on the structure, magnetic properties, Mössbauer parameters and some specific characteristics of ferrites were summarized. A method utilizing self-propagating high-temperature synthesis reactions (SHS), which provide an energy to overcome a solid state diffusion barrier internally, within the starting materials, by promoting an exothermic chemical reaction were offered. Supplementary heat treatments for all the samples were also used. A systematic decrease in lattice parameters with increasing chromium substitution was found to be independent of the lattice type. The so-called effect of elementary cell "compression", caused by applied magnetic field, were observed. Variations in the unit cell size may be attributed to smaller ionic radii of six fold coordinated  $\text{Cr}^{3+}$  compared to that six fold high-spin  $\text{Fe}^{3+}$  and anisotropy structuring during combustion in magnetic field. Magnetic characteristics (specific and remanent magnetization, coercivity) demonstrated significant changes with increasing Cr content, as well as after in-field experiments compare with no-field one. The Mössbauer spectra, recorded at room and liquid nitrogen temperature demonstrated increasing of sextets lines broadening and decreasing of effective magnetic field values in all the sublattices with Cr. Cr presence also lead to the

paramagnetic doublet or singlet formation in the middle spectra region. The spectral parameters of the same composition samples demonstrate significant difference after synthesis in magnetic field in compare with zero field experiments. The Curie temperatures for all the ferrites decreases but electric resistance increases with chromium content and after magnetic field using in the combustion experiments. Some other aspects - superstructures formation, crystallite sizes changes, FT-IR and UV- spectra, etc. - were also discussed.

This work is supported by Russian and Belorussian Foundations for Basic Researches, grant RFBR 00-03-81193 Bel2000\_a, Russian Foundation for Basic Research, grant RFBR 00-15-99054, 00-03-40141i.

### **O-1-61:Structure and Variability of Spinning Reaction Waves in Cylindrical Sample**

*Tatyana P. Ivleva, Alexander G. Merzhanov*

*Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences,  
Chernogolovka, Moscow region, 142432 Russia*

The spinning reaction wave is well-known type of wave, which has been found in many physical, chemical and biological systems. The spinning combustion front propagating through a solid-phase compound is typical example of such a wave. We consider a system of reaction-diffusion equations describing the propagation of combustion waves along a cylindrical sample of solid fuel. The solid flame is a complicated phenomenon. However, reaction and thermoconductivity play key roles. This is motivation for constructing our 3D model which accounts for diffusion of heat and first-order with respect to the limiting reactant, irreversible Arrhenius kinetics. The thermophysical properties (density, thermal conductivity, capacity) are assumed constant. Reaction is initiated at the upper face of the cylinder, so that it propagates downward. Chemical characteristics of reacting mixture are the reason of nonstability of propagation of the plane front with constant velocity. The mathematical model of the process was studied numerically by using the method of finite differences. The applied spatial grid was non-uniform with an unfixed number of nodes, and it was adapted to a solution.

We will illustrate the propagation of 3D periodic reaction waves. The mechanism of hot spots moving was described and analysed for many found modes. We will describe the propagation modes that have not yet observed experimentally. There are two kinds of modes: the modes with invariable front structure (at small sample radius) and the non-stationary modes with multiple transformations of the front during a period. In the latter case, blinking of hot spots is observed on the sample surface. Flickering of hot spots can be both synchronous and by-turn. The hot spots can move both in a right-side and left-side way. The non-uniqueness of combustion modes was found. The type of established propagation mode depends on the conditions of initiation. The areas of existence for these modes have been determined.

A chaotic mode also was found. In this case number of spots, their brightness and direction of moving changes. It was shown that heat loss can lead to self-organisation of front structure and chaotic mode can reform to periodic one.

The distribution of the mean (along the cylinder cross-section) temperature along the sample is similar to the distribution of the temperature at 1D stationary front propagation. The amplitude of the mean temperature oscillation is very low even at very high amplitude of temperature oscillations in the reaction zone on the cylinder axis and generatrix. This is associated with temperature redistribution along the sample cross-section forming the hot spots during 3D spinning combustion.

It was found that for the spinning combustion average velocity of the front propagation was approximately identical to the theoretical velocity of stationary combustion wave propagating through condensed phase under adiabatic conditions. The mean front velocity decreases slightly while sample radius increases.

## **O-2-40: Structure and Properties of Multicomponent Thin Films Based on the Systems Ti-Si-N and Ti-X-B-N (X=Al, Si or Cr) Deposited by Magnetron Sputtering Using SHS Targets**

*D.V. Shtansky<sup>1</sup>, A.N. Sheveiko<sup>1</sup>, E.A. Levashov<sup>1</sup>, S.A. Kulinich<sup>2</sup>, J.J. Moore<sup>3</sup>*

*<sup>1</sup>SHS-Center of the Moscow Steel and Alloys Institute and the Institute of Structural Macrokinetics and Materials Science Problems of RAS, Leninsky pr. 4, 164, Moscow 119991, Russia*

*<sup>2</sup>Department of Materials Engineering, Graduate School and Faculty of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan*

*<sup>3</sup>Center for Commercial Application of Combustion in Space (CCACS)  
Colorado School of Mines, Golden, CO, 80401, USA*

Films of Ti-Si-N and Ti-X-B-N (X = Al, Si, or Cr) were deposited by dc magnetron sputtering of composite targets (two-five phases) in a gaseous mixture of Ar + N<sub>2</sub>. The influence of the substrate temperature, bias voltage, and nitrogen partial pressure on the structure and properties of the films were studied. Composite targets for PVD were manufactured by means of self-propagating high-temperature synthesis (SHS) method.

The process of sputtering of composite targets both in an atmosphere of argon, and reactively, in a gaseous mixture of argon and nitrogen was studied. Microstructure and composition of films were studied by means of Auger electron spectroscopy (AES), secondary ion mass-spectroscopy (SIMS), X-ray photoelectron spectroscopy (XPS), X-ray diffraction, electron energy-loss spectroscopy (EELS), as well as both plain-view and cross-sectional conventional transmission electron microscopy (TEM) and high-resolution TEM.

The structure of Ti-Al-B-N films consisted of various nanocrystalline mixtures of (Ti, Al)N, TiB<sub>2</sub>, h-BN and c-BN phases in amorphous matrix. TiAl<sub>0.2</sub>B<sub>0.7</sub>N<sub>0.7</sub> film was shown to consist of crystalline clusters, 4-8 Å in size, being only one to three unit cells dimension. This is extremely small crystallite size, which has hitherto been reported, resulting in a significant fraction of atoms locating at the grain boundaries. Ti-Si-B-N films consisted of a mixture of hexagonal Ti(B, N)<sub>x</sub> nanocrystallites embedded in amorphous matrix. Ti-Si-N and Ti-Cr-B-N films deposited under similar conditions displayed NaCl-type structure with different morphologies: a columnar structure with a crystallite diameter in the range of 10-15 nm and an isotropic finely grained structure with a crystallite size of 3-7 nm, respectively. Particular attention was paid to the structure of grain boundaries in nanostructured thin films. The amorphous phase was shown to form as individual patches rather than as intergranular amorphous layers of uniform thickness. The films were characterized in terms of their microhardness, toughness, elastic modulus, elastic recovery, wear resistance, residual stress and a type of deformation. A strong correlation between the structure and properties of nanostructured films was outlined.

## **O-2-44: Structure and Properties of SHIM-Alloys and ESA-Coatings Strongly Modified by Nanosized Particles**

*O.V. Malochkin<sup>1</sup>, E.A. Levashov<sup>1</sup>, A.E. Kudryashov<sup>1</sup>, F. Gammel<sup>2</sup>, R. Suchentrunk<sup>3</sup>*

*<sup>1</sup>SHS-Center of the Moscow Steel and Alloys Institute and the Institute of Structural Macrokinetics and Materials Science Problems of RAS, Leninsky prospect, 4, 164, Moscow 119991, Russia*

*Phone: +(095) 230-4642, Fax: +(095) 236-5298*

*<sup>2</sup>Space Company, EADS, 81663 Munich, Germany*

*<sup>3</sup>Daimler-Chrysler AG, Research and Technology, 81663 Munich, Germany*

The main purpose of the proposed investigations is connected with the development of technology for novel SHS-composite ceramic materials production using various nanosized powders obtained by sol-gel synthesis and plasma-chemical method.

Nanosized powders were used as an addition to exothermic mixtures for production of synthetic hard instrumental materials (SHIM), targets for magnetron sputtering, and electrodes for electrospark alloying by force SHS-pressing technology.

Effects of nanosized powder additions on macrokinetics characteristics of combustion process and peculiarities of products phase- and structure formation in the combustion wave were investigated. The microstructure, phase composition and physical-mechanical properties of nanosized powders containing SHS-materials on the base of Ti-Cr-C-Ni and Ti-Al-B systems were studied.

The introduction of nanosized powders, such as  $ZrO_2$ ,  $Al_2O_3$ , NbC,  $Si_3N_4$ , W, WC, WC-Co as an inert additions, provides to change the phase composition of SHIM-3B and Ti-Al-B alloys, to improve the physical-mechanical properties (strength, hardness, and crack growth resistance  $K_{IC}$ ) due to modification of the SHS-material microstructure.

A complex study on the structure and the properties (thickness, continuity, microhardness, wear resistance) of electrospark coatings produced using nanosized powders containing SHS-electrode has been carried out.

#### **O-1-7: Structure of Ti-Al Powder Mixture Synthesis Product Realized in Condition of Thermal Explosion with Varied Heat Removal**

*V.Y. Philimonov, V.V. Evstigneev*

*Polzunov Altai State Technical University, Str. Lenina 46, Barnaul 656099 Russia*

*Tel: (8-385-2) 260917, 368463, Fax: (8-385-2) 367864, 368463.*

Traditional ways of obtaining combustion product having necessary composition and properties are as a rule connected with varying parameters of original mixture (porosity, powder particles size, initial components ratio< preheating and etc.,) since it is extremely complicated to operate combustion wave thermal structure. In the mode of thermal explosion there appears an additional mechanism of synthesis process control, connected with the possibility to change thermophysical situation of exothermic reaction course.

The given work demonstrates the possibility of control of intermetallic compounds (solid solution) structure and content in finite product by changing external thermal conditions of self-heating. It shows that synthesis maximum temperature and self-heating rate change with a different level of thermal insulation of machining attachment internal surface. By the method of X-ray phase analysis the direct correlation between synthesis modes and synthesized product content is determined. The analysis of thermograms for three insulation levels gave assessments of fusion time, heating and fusion time relation, synthesized product volume during the time of fusion. It was determined that in the period of fusion the depth of transformation and heating are not large, and self-heating mainly happens in collective conditions.

The results of the research allow to make a conclusion that the mechanism of synthesis kinetics control and, consequently, the control of the structure and phase content of finite product can be realized.

#### **O-2-151: Studies of Reaction and Solidification of Manufacture Process of Ceramic-Lined Composite Steel Pipes by SHS**

*S.-G. Zhang, X.-X. Zhou, D.-H. Qian*

*Nanjing University of Chemical Technology, Nanjing Jintao Wear Resistant Pipes Co., Ltd*

*Nanjing Keyuan Combustion Synthesis Technology Co., Ltd, 5 Jinchuanmenwai St, Nanjing, Jiangsu, 210015 People's Republic of China*

The adiabatic reaction temperature of  $Fe_2O_3 + 2Al = Al_2O_3 + 2Fe$  is 3622K, the actual temperature of the reaction is much higher than the melting points of the products. If the reaction takes place in a turning steel pipe, a centrifugal force makes the molten products alumina and iron separate and the alumina spreads on the inside wall of the steel pipe forming the ceramic-lined composite pipe.

Curves of temperature distribution of the ceramic layer, the metal layer, and the matrix pipe was established.

Spin combustion, an unsteady combustion mode was found during the termite reaction was propagating in the pipe.

### **O-3-158: Synthesis of Mg<sub>2</sub>Si via Thermal Explosion Mode of SHS: Experimental Observation and Modeling**

*D. Horvitz, L. Klinger, I. Gotman*

*Department of Materials Engineering, Technion, Haifa 32000, Israel*

Due to a number of outstanding physical and mechanical properties, magnesium silicide, Mg<sub>2</sub>Si is a potentially attractive material for various structural and functional applications. The production of this intermetallic compound, however, constitutes a major engineering problem due to the high Mg vapor pressure at the Mg<sub>2</sub>Si melting temperature making conventional casting difficult if not impossible.

In a related research it has been shown that combustion wave propagation is a feasible means of producing very pure Mg<sub>2</sub>Si powder. The thrust of the present work is experimental observation and modeling of the thermal explosion mode of SHS in Mg-Si blend. The model developed describes non-isothermal reactive diffusion in Mg-Si powder blends leading to thermal explosion under different conditions of heat transfer into the surrounding ambience. The model explicitly incorporates the kinetics of 2 Mg+Si $\rightarrow$ Mg<sub>2</sub>Si reaction that was experimentally measured in the present work for the isothermal growth of Mg<sub>2</sub>Si diffusion layer on the surface of Si wafer immersed into Mg powder. According to both experimental results and model predictions, Si powder particle size significantly affects the ignition of thermal explosion. When fine Si powder was used, thermal explosion was ignited at temperatures as low as 500°C, and the measured combustion temperature was above the melting point of Mg<sub>2</sub>Si (> 1100°C). As a result, a dense Mg<sub>2</sub>Si product was obtained. At the same time, no thermal explosion was observed for the coarse Si powder, quite in agreement with the model predictions.

### **O-1-101: The Synthesis of Sulfides in Combustion Regime**

*R.K. Tukhtaev<sup>1</sup>, V.V. Boldyrev<sup>1</sup>, A.I. Gavrilov<sup>1</sup>, S.V. Larionov<sup>2</sup>*

<sup>1</sup>*Institute of Solid State Chemistry, Russian Academy of Sciences Siberian Branch, Novosibirsk, Russia, e-mail: [tukhtaev@solid.nsc.ru](mailto:tukhtaev@solid.nsc.ru)*

<sup>2</sup>*Institute of Inorganic Chemistry, Russian Academy of Sciences, Siberian Branch, Novosibirsk, Russia*

The possibility to synthesize metal sulfides in combustion of mixtures composed of an oxidizer and fuel is investigated. Nitrates and oxides of metals were used as oxidizing agents; ammonium rhodanide or sulfur-containing organic derivatives of ammonia and hydrazine (thiocarbamide, thiosemicarbazide, thiocarbohydrazide, thioacetamide) were used as fuel.

The investigated mixtures are able to provide self-maintained combustion with components ratio varied within a wide range. Depending on mixture composition, final products can be oxides, sulfides or metal. In order to obtain sulfides, the composition of the mixtures should meet definite requirements. In the present study we have determined concentration limits of the mixtures within which the combustion is accompanied by the formation of sulfides alone.

Unlike the combustion of complex compounds of metal nitrates with thiocarbamide and thiosemicarbazide [1,2], the proposed method allows governing the dispersity and morphology of the resulting sulfides not only by changing the external pressure but also by changing the component ratio of the mixture.

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#### **O-1-225: Effect of Hot-Spots and Substrates Composition on the Microstructure of Powders Produced During MW-SHS of SiC**

*D. Kuzmenko<sup>1,3</sup>, T. Chudoba<sup>1</sup>, W. Lojkowski<sup>1</sup>, J. Binner<sup>2</sup>, T. Cross<sup>3</sup>, D. Kolesnikov<sup>1</sup> and E. Grzanka<sup>1</sup>*

*<sup>1</sup> High Pressure Research Center of PASC, 29/37 Sokolowska str., 01-142, Warsaw, Poland*

*<sup>2</sup> IPTME, Loughborough University, Leicestershire, LE11 3TU, UK*

*<sup>3</sup> School of Electrical & Electronics Engineering, The University of Nottingham, University Park, Nottingham NG7 2RD, UK*

SHS - Self-Propagating High-Temperature Synthesis ignited by microwaves can be used to produce SiC powders via the reaction of silicon and carbon black powders. Once initiated, the exothermic reaction  $\text{Si} + \text{C} \rightarrow \text{SiC}$  propagates in a self-sustaining mode through the reaction batch. The potential advantages of the microwaves ignited SHS technology are the high purity of the powders, low energy consumption and fine grain size. There are still difficulties as far as controlling the product uniformity and grain size.

We have shown that a special microwave reactor with a well-defined hot spot distribution provides additional flexibility for controlling the reaction. Proper positioning of the hot spots in relation to the precursor mix permitted us to optimize the point of ignition and gave better control over propagation of the reaction. As a consequence, the fraction of nanocrystalline powders in the reaction product has been maximized.

We have also studied the microwave absorption as a function of the mixture composition, with the aim of better understanding the absorption mechanism and optimization of the fraction of nanocrystalline powder in the product.

#### **O-3-92: Theoretical and Technological Aspects of Synthesis of Nano- and Micro-Crystal Composite Powders and Prospects of Their Industrial Application**

*P.A. Vityaz<sup>1</sup>, A.Ph. Ilyuschenko<sup>2</sup>, A.V. Beliaev<sup>2</sup>, T.L. Talaka<sup>2</sup>*

*<sup>1</sup>National Academy of Sciences of Belarus and Powder Metallurgy, Research Institute with Pilot Plant, Minsk, Belarus*

*<sup>2</sup>Powder Metallurgy Research Institute with Pilot Plant, Minsk, Belarus*

In the last years much interest has been paid to materials structurized in nano- and micro-metrical range of sizes. Comparability of geometrical sizes and characteristic size for a physical phenomenon under consideration (length of electrons or phonons free run, size of electrical or magnetic domain, length of crystal lattice defects as dislocations or declinations) causes different size effects, and increased surface energy and extreme conditions of nano-particles formation lead to metastable condition of materials that are in ultra-disperse state. In particular, physical peculiarities of ultra-disperse conditions realize in a significant increase of strength properties of nano-structural materials with conservation of high plasticity and low threshold of cold shortness, semiconductor type of conductivity, supermagnetism, increase of temperature of transformation into superconductive state, change of optical characteristics, etc.

Some theoretical and technological aspects of creation sub-microstructural composite powders for different purposes and fields of their application are under discussion.

A structure-forming basis of nano-composites, as a rule, consists of high- and ultra-disperse particles with sizes of 5-500 nm. It was determined that comparatively low additions of powders like that can significantly improve structure and properties of matrix materials (metals, alloys, polymers, ceramics, etc.). Production of ultra-disperse powders belongs to so called «hi-tech» group, and high-energy synthesis methods including detonation processes with mixture blasting

agents, mechanical-chemical technologies, combined with mechanical activation or blasting treatment of SHS.

A list of papers on this problem from Belarus is attached. Some prospects of industrial application of the developed materials are discussed. Successful development of industrial capacities for production ultra-disperse diamonds with different phase compositions (cubic diamond - amorphous carbon), degree of purity, value and sign of surface discharge, and also composite metal-ceramic SHS - powders enabled to move on, from laboratory testing to industrial technologies of application of these materials in most important industries, such as: machine-building and metal treatment, transportation, radio and electronic industry, production of consumer goods.

## **O-2-232: Some features of gasless combustion and product structure**

**formation in the nano-scale multilayered intermetallic films***E.H.*

*Grigoryan<sup>1</sup>, N.G.Elistratov<sup>2</sup>, D.Yu.Kovalev<sup>1</sup>, A.G.Merzhanov<sup>1</sup>, A.N.Nosyrev<sup>2</sup>, V.I.Ponomarev<sup>1</sup>, A.S.Rogachev<sup>1</sup>, V.I.Khvesyuk<sup>2</sup>, and P.A.Tsygankov<sup>2</sup>*

<sup>1</sup>Institute of Structural MacrokINETICS and Materials Science RAS

<sup>2</sup>Moscow State Technical University

Multilayered Ti/Al nano-films were obtained by plasma-assisted sputtering technique. Thickness of the alternate layers of Al and Ti was from 5 to 100 nm, a total number of the layers 300- 2000, so that total thickness of multilayered films was 15-20 micron. Gasless reaction waves were initiated in the samples by short local heat impulse or by means of uniform heating of the film right up to self-ignition in vacuum. Temperature of self-ignition turned out to be about 590-640 K, which is much less than self-ignition temperature of powder mixture (~940 K). Characteristic features of wave propagation have been studied depending on average composition, thickness of nano-layers, initial temperature of the samples. Oscillating and stationary regimes of combustion were observed. Mechanism of solid product structure formation has been analyzed. New effect of "inheritance" of initial crystallographic textures by solid products of combustion has been found.

Some possible explanations for this new phenomenon are suggested.

This work is supported by Russian Foundation of Basic Research (grant 01-03-33017).

## **O-1-231: Synthesis of Dense Light Weight Al<sub>3</sub>Ti/B<sub>4</sub>C Composites by Pressure-assisted Thermal Explosion**

*S. Zamir, I. Gotman, E.Y. Gutmanas*

*Department of Materials Engineering, Technion, Haifa 32000, Israel*

Al<sub>3</sub>Ti/B<sub>4</sub>C composites are potential substitutes for the currently used pure B<sub>4</sub>C in the light-weight armor applications due to the high hardness and strength-to-weight ratio of the titanium aluminide. Self-propagating High-temperature Synthesis (SHS) utilizing the exothermic heat of the 3Al+Ti→Al<sub>3</sub>Ti reaction could become an attractive route of in situ processing of Al<sub>3</sub>Ti/B<sub>4</sub>C composites.

In the present research, dense Al<sub>3</sub>Ti/B<sub>4</sub>C composites containing up to 45 vol.% B<sub>4</sub>C were synthesized from a fine attrition milled Ti-3Al powder blend diluted with a coarse B<sub>4</sub>C powder employing a recently developed SHS-based Reactive Forging method. Green Ti-Al-B<sub>4</sub>C compacts were placed between preheated press rams and thermal explosion (SHS) was ignited at ram temperatures as low as 800°C. The temperature of the samples in the course of combustion synthesis was accurately monitored. The application of a relatively low pressure during thermal explosion resulted in full densification of thus synthesized Al<sub>3</sub>Ti/B<sub>4</sub>C composites. The microstructure of the samples obtained was characterized by x-ray diffraction and scanning electron microscopy with chemical analysis (SEM/EDS). Due to the very short SHS processing time (less than 1 min), no undesirable reaction products were formed at the B<sub>4</sub>C particles/Al<sub>3</sub>Ti matrix interface.

## POSTERS

### P-2-173: Feasibility of Synthesis of Dense Nanomaterials from Mechanically Activated Powders

*F. Bernard<sup>1</sup>; F. Charlot<sup>1,2</sup>, S. Paris<sup>1,2</sup>; Ch. Gras<sup>1,2</sup>, E. Gaffet<sup>2</sup>, Z.A. Munir<sup>3</sup>*

*<sup>1</sup>LRRS, UMR5613 CNRS-University of Burgundy, BP 47870 21078 Dijon, France*

*<sup>2</sup>Far from Equilibrium Transitions Phases Group, CNRS UPR 806 90010 Belfort, France*

*<sup>3</sup>Department of Chemical Engineering and Materials Science, University of California, Davis CA 95616, USA*

A new method to form nanomaterials, the mechanically-activated SHS process (MASHS), has been recently investigated [1,2]. Reactant powders were co-milled in a special high-energy planetary ball mill, developed by Gaffet [3]. In this mill the disk rotation speed and the vial rotation speed can be independently controlled. Under such conditions the shock frequency and shock energy can be determined to mechanically activate the reactant powders. After this mechanical activation, each micrometer-scale powder particle was found to be composed of nanostructured reactant grains. Regular SHS were performed on these mechanically-activated powders and the products were found to be also nano-scaled.

Although the SHS reaction retains the nanostructure obtained by the mechanical activation step, the product is porous, a typical circumstance in view of the sources of porosity in SHS as reported previously [4]. The porous nature of SHS products is a major hurdle to the application of the nanomaterials obtained by MASHS. The purpose of this work is to investigate the feasibility of forming dense Fe/Al or Mo/Si nanomaterials by the use of the field-activated pressure-assisted synthesis method developed by Munir [5]. Mechanically-activated reactant powders were placed inside a graphite die and subjected to a uniaxial pressure while a high level electric current is passed through the die. After the synthesis reaction, the samples had relative densities greater than 95 %. The products were the desired phases (FeAl and MoSi<sub>2</sub>) with little or no secondary phases. The microstructure of the products was investigated by XRD techniques to determine the crystallite size. The preliminary results indicate that the products of these two materials are nanocrystalline, suggesting that this technique can provide a new route to the formation of dense nanomaterials where the consolidation and synthesis steps are accomplished simultaneously.

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### P-2-170: Activation of Green Mixtures with Electromagnetic Field

*V.A. Veretennikov<sup>1</sup>, D.I. Slovetskii<sup>2</sup>, V.T. Popov<sup>2</sup>, S.E. Zakiev<sup>1</sup>,*

*Yu.G. Morozov<sup>1</sup>, M.V. Kuznetsov<sup>1</sup>*

*<sup>1</sup>Institute of Structural Macrokinetics and Materials Science, RAS, Chernogolovka, Moscow Region, 142432 Russia*

*<sup>2</sup>Topchiev Institute of Petrochemical Synthesis, RAS, LENINSKII PR. 29, MOSCOW, 117071, RUSSIA*

The effect of electromagnetic field on burning SHS system is well known. Meanwhile, modification of green mixture under the action of applied field has not yet been explored so far. The most popular methods of green mixture pretreatment are mechanoactivation, thermal treatment, and chemical activation (e.g. cladding). Preparation of green mixtures with a desired mesostructure still remains to be a problem. Nevertheless, the extent of coagulation (close contact

between reagent particles) in a green mixture is known to affect the physical properties of a pellet (e.g. its thermal conductivity). Pretreatment of starting materials with electromagnetic field may be expected to open an opportunity for solution of the problem.

In this work we examined the action of pulsed magnetic field ( $H = 10^6$  A/m, repetition frequency around 700 Hz, pulse energy 3 kJ) on the mesostructure of carbon-containing powders. Such a treatment was found to change the mesostructure and, accordingly, physicochemical properties of material: the reactivity of carbon black increased by a factor about 20% while the electric conductivity, by 20–30%. The obtained data seem promising for realization of the memory effect in SHS products. The effect may also turn out useful for controlling SHS reactions and product characteristics.

This work was supported by the Russian Foundation for Basic Research (project no. 01-03-32683a).

#### **P-2-24: Advanced (New) Ceramics. SHS R&D Standardization**

V.K. Prokudina, M.A. Nasonova, T.N. Shtenberg

*Institute of Structural Macrokinetics and Materials Science, RAS, CHERNOGOLOVKA, RUSSIA*

In reference books the term "Advanced (new) ceramics" is considered as a new generation of ceramic materials. Unlike traditional ceramics obtained from synthetic raw materials as a rule (for example, from refractory compounds) these compounds are manufactured by means of new technology-intensive methods of sintering and can be used in up-to-date engineering.

The term "SHS ceramics" quite fits the definition given above. But it has a small addition: the ceramics can be obtained both by the direct SHS method and by SHS material processing.

The report is dedicated to standardization of R&D concerning SHS ceramics, namely to establishment of engineering standards, regulations and requirements to products, their production technologies, control methods (tests), etc.

The order of the report presentation corresponds to the classification of SHS ceramics according to its properties and application, namely:

- for tools;
- for coatings (including coatings themselves and electrodes for their surfacing);
- abrasive materials and tools;
- refractory materials;
- construction ceramics (including friction, composite, anti-friction wear-resistant, corrosion-resistant, and some other materials for machinery);
- for filters (porous ceramics).

For each kind of SHS ceramics the review on State Standard search for analogous products has been carried out. It was shown that the most number of standards was designed for refractory, construction ceramics and for ceramics for coatings.

Practically all types of State Standards (technical specifications, index nomenclature, control methods, etc.) were found for these types of ceramics.

Ceramics for filters clearing water is not described in State Standards at all, though the manufacture of these filters is developed very quickly.

SHS-ceramics is presented both as separate developments, and as homogeneous types of products. The main technical characteristics, application fields, and standardization data are given for SHS-ceramics. Comparison with analogous products is made for laboratory samples. Information on normative-technical documentation, production output, and certification availability is given for the products manufactured as pilot scale batches or on an industrial scale.

This work is supported by Russian Foundation for Basic Research, grant RFBR 00-15-99054.

## P-1-82: Analysis of the Critical Conditions of Ignition of Gas-Suspended Solid Fuel with a Heated Surface

B.S. Septyarskii, T.P. Ivleva

*Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences,  
Chernogolovka, 142 432 Russia, e-mail: [sepl@ism.ac.ru](mailto:sepl@ism.ac.ru)*

The present paper reports the results of the theoretical analysis of the process of ignition of gaseous suspensions with a heated body.

The following model process is considered. At  $t = 0$ , a surface heated up to  $T_{ig}$  ( $T_{ig} > T_0$ ) is brought to contact with a homogeneous gaseous suspension ( $T_0$ ) containing  $N$  particles per volume unit. At  $t = t_{pul}$ , the surface is drawn away so that at  $t > t_{pul}$  the gas suspension is considered to be heat-insulated. At  $0 < t < t_{pul}$ , the temperature gradient causes conductive heating of the gas, which in turn warms up the solid particles. The particle temperature growth entails a sharp increase in the rate of heterogeneous interaction of the particles and the oxidant contained in the gas, which can result in the gas suspension ignition. The process is described by a two-dimensional mathematical model suggesting the difference between the particle and gas temperatures. The study was aimed at determination of such  $t_{pul} = t_{cr}$  value as a function of the governing parameters that at  $t_{pul} > t_{cr}$  the gas suspension is ignited, *i.e.* the combustion wave propagation is initiated, while at  $t_{pul} < t_{cr}$  the process of chemical conversion could be stagnated.

An earlier performed criterial analysis of the starting set of equations for  $t_{pul} \rightarrow \infty$  showed that dependent on the ratio of the characteristic time of the heat exchange between the particles and the gas  $t_z$  to that of the chemical reaction  $t_{ch}$  there could occur two different regimes of ignition. If  $t_z$  is  $e$  (2.72) or more times is higher than  $t_{ch}$  (high ignition temperatures, low values of the parameter  $z = t_{ch}/t_z$ ) the process of ignition proceeds via the diffusion mechanism. At  $t_{ch} > t_z$  (the duration of the heat exchange is lower than the reaction characteristic time), the kinetic regime of ignition is observed, *i.e.* the suspension is ignited at the same particle and gas temperatures and the process can be described with a one-temperature model. The specific features of both regimes were analyzed with the use of the wave theory of ignition (WTI). According to WTI, the time characteristics of ignition are presented via the parameters of the intermediate combustion wave ICW, which is a steady-state combustion wave with a maximum gas temperature equal to that of ignition. The dependencies of the time characteristics of ignition on the major parameters of the process (the particle mass concentration in the gas, the particle size, the kinetic characteristics of the reaction, the ignition temperature) were described by simple expressions.

In accord with the ideas of WTI,  $t_{cr} = t_0$ , where  $t_0$  is the time of the zero gradient establishment on the suspension-heater interface at  $t_{pul} \rightarrow \infty$ . As shown by the results of numeric calculations,  $t_{cr} = t_0$  for the kinetic (one-temperature) regime of ignition, while in the diffusion regime ignition could be expected at  $t_{pul} < t_0$ . The result is the consequence of the absence of the positive reverse relation between the heat release rate and the particle temperature in the diffusion regime of interaction and the hysteresis of the ignition and stagnation conditions characteristic of the particle interaction in the oxidant medium. The more detailed calculations showed that the minimum heat accumulated in the system by the moment of ignition and, consequently, the minimum ignition time can be achieved at  $t_{pul} = t_0$ . The formulas for the ignition delay time and the critical conditions of ignition at  $t_{pul} < t_0$  were derived.

The study was supported by RFBR (Grant 00-03-32034) and INTAS –ESA (Grant 99-0138).

## P-1-144: Anomalous Behavior of High-Temperature Resistivity in Nitride SHS-Ceramics

A.V. Karpov, I.P. Borovinskaya, Yu.G. Morozov, V.A. Bunin, M.V. Kuznetsov

*Institute of Structural Macrokinetics and Materials Science RAS, Chernogolovka,  
142432 Russia*

*Tel: 007 (09652) 46317, Fax: 007 (095) 9628025, E-mail: [karpov@ism.ac.ru](mailto:karpov@ism.ac.ru)*

The ceramic materials on the basis of aluminum nitride and titanium diboride have the relevant operational use as effective heating elements in devices of vacuum evaporation of aluminum. The

purpose of our examinations was the study of specific resistance of such ceramics obtained by method of self-propagating high-temperature synthesis in high temperature region.

Samples for study was synthesized with usage of aluminum and nitrogen, as fissile components of reaction with adding titanium diboride and aluminum nitride as diluents, which one attached an explored composition the relevant conductive properties. X-ray analysis was shown, the obtained samples contained aluminum nitride and titanium diboride as main components and can be divided into two groups: R1 - the samples containing in a final product free aluminum as impurities and R2 - the samples containing in a final product titanium nitride and boron nitride.

The electrical measurements were carried out in vacuum ( $10^{-3}$  Pa) by using the conventional 4-probe method in temperature range 300-1300 K. The hysteresis behavior of the specific resistance for the samples from group R1 was observed. The shapes of the heating curves were depends on the titanium diboride content in the samples. The sharp variation of the specific resistance at temperature according to the melting point of aluminum for the samples belonging to group R2 was discovered. We failed to detect the hysteresis effects in resistivity for the samples of this group upon heating and cooling. The explanation of probable mechanisms of hysteresis effects are given. This work is supported by Russian Foundation for Basic Research, grants RFBR 00-03-32481a, 00-15-99054P-2-94:

Applications of a Combustion Synthesized AlN Powder for High Thermal Conductivity Materials

*Shyan-Lung Chung, Ming-Lung Chou, Chun-Hung Chen, Huei-Chung Chen*

*Department of Chemical Engineering National Cheng Kung University*

*Tainan, Taiwan, 70101 ROC, E-mail: [slchung@mail.ncku.edu.tw](mailto:slchung@mail.ncku.edu.tw)*

An AlN powder synthesized using a combustion synthesis method was tested for its feasibility to fabricate high thermal conductivity materials including densified bodies and AlN/polymer composites. This combustion synthesis method is characterized by low production cost, high production rate, capability for scaling up, high product yield, and high purity of the AlN product powder. In this method, Al powder and N<sub>2</sub> gas were used as the raw materials. For a batch of 3 Kg Al powder, it required ~1000 W of heating for ~1 min to ignite the combustion reaction and it took ~30 min to complete the combustion. The largest batch that has been synthesized is 70 Kg of AlN powder. The AlN powder was sintered by using electric furnaces. The sinterability of the AlN powder and the thermal conductivity of the sintered bodies were compared to those of commercial powders. The AlN powder was also tested for fabricating epoxy-molding compounds (EMC) which has potential for use as electronic packaging materials. The thermal conductivity of the EMC was also compared to that from commercial AlN powders.

#### **P-1-183: Application of the Synchrotron Radiation for Dynamics Study of SHS-Processes**

*E.B. Pis'menskaya<sup>1</sup>, A.S. Rogachev<sup>1</sup>, V.V. Aleksandrov<sup>1</sup>,*

*B.P. Tolochko<sup>2</sup>, M.R. Sharafutdinov<sup>2</sup>, O.V. Evdokov<sup>2</sup>, D.Y. Naumov<sup>2</sup>*

*<sup>1</sup>Institute of Structural MacrokINETics and Materials Science RAS, Chernogolovka*

*<sup>2</sup>Institute of Nuclear Physics SB RAS, Novosibirsk*

New results concerning time-resolved X-ray diffraction using Synchrotron radiation are reported. The idea of the work is to modify experimental set-up and scheme of the measurement in order to decrease measuring time down to 1 ms. In contrast with the previous experiments, measuring area was parallel to combustion front. The position of monochromator was also changed, which allow us to increase the intensity of X-ray beam by about 1000 times. Thus, we studied SHS reaction between aluminum and nickel powders with time resolution of 5 ms. We observed the reaction of the wave propagation immediately and the next stage of conversion: at the beginning Al is melt, than Ni is melt, and NiAl are formed. The first crystals appear during 10-15 ms after passing of the combustion front. Some previous results for the system Ti-Si was also obtained.

### P-2-193: Ba-Ti-Citrate Sol-gel Autoigniting Synthesis of BaTiO<sub>3</sub> Nanopowder

Fang-Ren Hu, Chang-Chun Ge

Laboratory of Special Ceramics and Powder Metallurgy

University of Science and technology Beijing, Beijing 100083, China

Sol-gel autoigniting synthesis (SAS) refers to a low-temperature self-sustaining combustion synthesis process in which oxidation-reduction reaction occurs during heating of gel derived from organic salt gel or organic salt with metal nitrate and a large amount of gases evolves. Compared with other processes for synthesizing oxide and complex oxide, it has several advantages such as: (1) low autoigniting temperature (150-350°C); (2) low combustion flame temperature (1000-1400°C); (3) mixing of compositions in atom or molecule level; (4) rapid reaction (within 1-3 minutes); (5) frail combustion product with high purity and numerous nano-porosity; (6) energy saving; (7) simple process.

Autoigniting synthesis of gel from Ba(NO<sub>3</sub>)<sub>2</sub>, TiO(NO<sub>3</sub>)<sub>2</sub> and C<sub>6</sub>H<sub>7</sub>O<sub>8</sub>·H<sub>2</sub>O aqueous solution was investigated at an initial temperature of 600°C and tetragonal BaTiO<sub>3</sub> nanopowder with particle size of 80 nm was prepared. It is indicated that the specific surface of the combustion product before and after calcination was 14.74 m<sup>2</sup>/g and 12.49 m<sup>2</sup>/g, respectively. The combustion involves solid phase reaction zone and gas phase flame reaction zone. The combustion flame temperature was 1123 K derived from thermocouple measurement.

**Key words:** Sol-gel Autoigniting Synthesis; Barium Titanate

### P-1-36: A Combinatorial Approach to Surface Contacts in Solid-Phase Reactions

C. Richter, H.J. Viljoen

Department of Chemical Engineering

University of Nebraska Lincoln, NE 68588-0126 USA

Macro-kinetic models for solid phase reactions require information about the contact area between reactants. A classical probability is presented to calculate the expectancy value for contact between two specified species when three different species are present in the system. Consider the generic reaction  $aA(s) + bB(s) \rightarrow cC(s, g)$ . The expectancy value depends on the surface area densities  $\sigma_i = N_i v$  where  $N_i$  denotes the particle density of species  $i$  and  $v_i$  is the volume per particle. The particles' surfaces are mathematically 'covered' by small tiles, associated with the species Bohr radius. A bijective mapping of all tiles (except onto itself) provides statistical expectations for contact between reactants. Competition exists between all six possible types of contacts and the contacts  $A - B$  constitute ones that are favorable for chemical reaction. To include the important role of particle geometry, the reactants are modeled as rectangular rhombi. The differences in reaction rate are investigated for cubes (quasi-spheres), platelets and needles by adjusting the aspect ratios. As the reaction proceeds reactants are consumed and products form that change the probabilities for reactant contacts. The evolution of particle sizes must be tracked and mechanisms that affect particle sizes must be included in the model. The dimensions change with reaction, compression and fracture. Fracture is described by the Hiramatsu-Oko equation that relates bed pressure with an equilibrium dimension. Compression requires an expression for the elastic potential energy of solid species and the Shchetinin equation is used. The particle size of the product depends specifically on the reaction mechanism. In the case of solid phase product, the tracking of product particle size becomes complicated, when the product is gaseous, the gas fills pores and they are treated within the combinatorial problem as 'particles' too. The model is illustrated for a i) gas product and ii) solid product. Factors that influence the reaction rate are initial particle sizes, aspect ratios, fracture criteria and stoichiometry. Surprising results are found. All the trends that have been observed are consistent with the competition that exists between contacts and the factors that influence the outcome of successful contacts. Any process that

increases the surface area density of the minority species (lowest statistical probability for contact) would lead to an enhancement of the reaction rate. If an increased reaction rate is the objective, it could be accomplished in a variety of ways, as demonstrated in the example. Reducing the particle size of the minority species, large aspect ratios of particles (platelets or needles instead of cubes) and non-stoichiometric mixtures shifted towards higher concentration of the minority species all contribute towards higher reaction rates. There is a growing awareness of the important role of mechano-chemical coupling. Fracture is a form of this coupling and its effect on reaction rate is shown to be very important.

#### **P-1-112: Combustion Model with an Electric Charge Formation**

*Igor Filimonov<sup>1</sup>, Mikael Nersessyan<sup>1,2</sup>, Dan Luss<sup>2</sup>*

*<sup>1</sup>Institute of Structural Macrokinetics and Materials Science RAS, Chernogolovka 142432 Russia*

*<sup>2</sup>Department of Chemical Engineering, University of Houston, Houston, TX 77204-4792*

A mathematical model of electric potential formation during solid state combustion has been developed. The model is based on the assumption that an electric charge is formed due to a gradient in the concentration of oxygen ions diffusing across an exterior layer of the product oxide. This leads to formation of a double-charge layer and electric voltage generation in the particle. The effects of infiltration, heterogeneous reaction kinetics, temperature difference between the condensed and gas phases on variation of the potential in course of the combustion wave passage through the single particle have been studied.

On the macroscopic level (at the scales  $\propto$  the sample size) the model treats the reactant porous medium as two interpenetrating continuums corresponding to the condensed and gas phases with the help of sufficiently general equations of infiltration combustion. Owing to large difference in densities between solid and gas phases it is assumed that all heat released during heterogeneous chemical reaction is completely absorbed by the condensed phase.

Computation of the electric voltage induced in the combustion wave consists of a simultaneous solution of the equations describing the microscopic (particles) and macroscopic level by an iterative procedure. Starting by calculation of the profiles for the macroscopic state variables (temperature, oxygen gas phase concentration, and metal conversion) in the combustion front we assume some quasi-stationary distribution of electric potential in the combustion wave. The predicted profiles of the macroscopic variables are used as boundary values in the solution of the single particle problems in the combustion front and post-combustion zone. The predicted distributions of oxygen ion concentration across the oxide layer within the reacting particles provide prediction by the modified Nernst equation of the corresponding electric potential. The new quasi-stationary distribution of electric potential is used to calculate a modified profile of macroscopic variables. These iterative calculations are continued till convergence is obtained. The model predicts the combustion wave velocity and the profiles of voltage, temperature, oxygen concentration and metal conversion within the combustion and post-combustion zones.

This work is supported by the NSF Grant #CTS-0003015

#### **P-1-159: Combustion Synthesis of $\text{Al}_2\text{O}_3$ -Ti Aluminide Composites: Effect of Starting Composition**

*D. Horvitz, I. Gotman*

*Department of Materials Engineering, Technion, Haifa 32000, Israel*

Interpenetrating alumina matrix composites toughened by different volume fractions of Ti aluminides were synthesized via thermal explosion of  $\text{TiO}_2$ -Al powder blends of varying stoichiometry. In order to overcome high porosity inherent in SHS products and to obtain dense materials, thermal explosion was performed under a moderate uni-axial pressure (Reactive Forging).

It has been previously reported that Reactive Forging of the  $TiO_2$ -Al powder blend with 3:7  $TiO_2$ -to-Al ratio yields a near fully dense  $TiAl$ - $Al_2O_3$  composite with a small amount of  $Ti_3Al$ . In the present research, the effect of changing the  $TiO_2$ -to-Al ratio on the ignition and course of SHS process, composition of the final products, their density and morphology has been studied. Thermodynamic estimations of combustion temperatures and liquid phase fractions during SHS processing were performed. Temperature evolution during processing was accurately monitored by several thermocouples. Materials obtained were characterized employing x-ray diffraction and SEM/EDS.

The results of the research show that, by increasing or decreasing  $TiO_2$ -to-Al ratio in the blend,  $Al_2O_3$ - $Ti_3Al$ /Ti and  $Al_2O_3$ - $TiAl_2$ / $TiAl_3$  composites, respectively, can be synthesized. The mechanical testing and microhardness measurements performed on the composites yielded a wide range of properties illustrating the  $Al_2O_3$ - $Ti_xAl_y$  system flexibility. The temperature evolution curves measured during thermal explosion provide invaluable data on reaction kinetics that will be further incorporated in the generalized model of reactive synthesis in the Al-Ti-O system.

#### **P-2-118: Combustion Synthesis of Aluminum Oxynitride and TIALON Powder**

*Berthold Liebig, Jan A. Puszynski*

*Chemistry and Chemical Engineering Department, South Dakota School of Mines and Technology, 501 E. St. Joseph Street, Rapid City, SD 57701, USA, Tel: 605/394-1230  
Fax: 605/394-1232, E-mail: [Jan.Puszynski@sdsmt.edu](mailto:Jan.Puszynski@sdsmt.edu)*

It has been demonstrated that aluminum nitride formed in a self-propagating high-temperature regime exhibits wurzite structure. By introducing oxygen into the Al-N-system, polytypoids or pure alon phase with spinel structure can be formed. Spinel ceramics, depending on their chemical structure, can be used as magnetic or semiconductor materials. Alon spinel is an attractive material for refractories and optical systems due to its chemical stability and transparency at high temperatures. Along spinels, when fully dense, becomes transparent. Its mechanical and optical properties make this material an excellent candidate for applications, where infrared or visible light windows are needed.

This paper will present experimental studies of the synthesis of alon materials in a combustion regime. The direct reaction between aluminum and nitrogen in the presence of a stoichiometric amount of alumina is not self-sustaining without a significant preheating. Previously it was demonstrated that alon powders can be synthesized by combusting aluminum powders in air or oxygen in the presence of aluminum nitride and/or alumina. Recently, it was found that such powders can be formed when aluminum powder reacts with oxygen-containing solid reactants in the presence of gaseous nitrogen. The effect of combustion conditions, such as pressure, gas atmosphere, oxygen-containing additives, and dilution will be presented and discussed. Combustion synthesized powders will be characterized both by X-ray diffraction, SEM, and Raman techniques.

The paper will also present recent experimental results on the formation of TIALON materials in a self-sustaining combustion regime.

#### **P-2-43: Development and Industrial Application of New SHS-Electrode Materials for Electrospark Alloying Technologies**

*A.E. Kudryashov<sup>1</sup>, E.A. Levashov<sup>1</sup>, E.I. Kharlamov<sup>1</sup>,*

*A.N Sheveiko<sup>1</sup>, A.M. Stolin<sup>1</sup>, I.I. Tsipin<sup>1</sup>, M. Trtanj<sup>2</sup>, M. Todorovich<sup>2</sup>*

*<sup>1</sup>SHS-Center of Moscow Steel and Alloys Institute (Technological University) and the Institute of Structural Macrokinetics and Material Science of RAS, Leninsky prospect, 4, 164, Moscow, 119991, Russia*

*<sup>2</sup>Institute for Nuclear Science "VINCA", Belgrade, Yugoslavia*

At the present time, the electrospark alloying (ESA) is one of the effective and available methods for machine part and instrument surface strengthening.

Development of new electrode materials compositions and upgrade of existing equipment considerably expand a range of application of the electrospark technology in the industry.

The follow aspects are presented in paper:

- surface strengthening of 5KhNM steel, widely used in the die forging, by electrode materials on the base of SHIM-3B modified by zirconium dioxide ( $ZrO_2$ ) additions;
- surface strengthening of EK61 nickel alloy, used in the aircraft industry, by different SHS-electrode materials as well as by conventional VK 8 and T15K6 hard alloys;
- surface hardening of gradient ledeburitic steels, used at the ore mining and processing enterprises for ore concentrate milling, by new SHS and TRESS electrodes.

The mass transfer of the new SHS electrode materials was investigated on various substrate cathodes. The complex of materials science studies of the coatings is carried out. Wear resistance of the coatings, optimal conditions of the application process during ESA-surfacing, and optimal electrode material compositions for every substrate were determined.

It was established that the (Ti+Al) and (Ni+Al) TRESS-electrodes in steel sheathes show the largest mass transfer, with thickness of the coatings reaching 150-200  $\mu\text{m}$ . The coatings produced by SHS-electrodes such as SHIM-3B with additions of nanocrystalline  $ZrO_2$  (particle size is  $\sim 10$  nm), SHIM-4 as well as VK 8 and T15K6 alloys have the highest wear resistance and microhardness.

#### **P-2-42: Deposition of Diamond Films on SHS-Diamond Containing Composites**

*E.A. Levashov<sup>1</sup>, V.G. Ralchenko<sup>2</sup>, B.V. Spitsyn<sup>3</sup>, M. Ohyanagi<sup>4</sup>, S. Hosomi<sup>5</sup>, M. Koizumi<sup>4</sup>*

*<sup>1</sup>SHS-Center of the Moscow Steel and Alloys Institute (Technological University) and the Institute of Structural Macrokinetics and Material Science of RAS Leninsky prospect, 4, 164, Moscow 119991, Russia, Phone: +(095) 230-4500, Fax: +(095) 236-5298*

*<sup>2</sup>General Physics Institute of RAS, ul. Vavilova, 38, Moscow 117942, Russia*

*<sup>3</sup>Institute of Physical Chemistry of RAS, Leninsky prospect, 31, Moscow 117915, Russia*

*<sup>4</sup>High-tech Research Center and Dept. of Materials Chemistry Faculty of Science and Technology, Ryukoku University, Ohtsu 520-21, Japan*

*<sup>5</sup>Tomei Diamond Co., Ltd., Joto 4-5-1 Oyama-city, 323, Japan*

Chemical Vapor Deposition (CVD) on functionally graded diamond containing composites is one of the effective method to produce thick diamond coatings with high adhesion strength. The force SHS – pressing technology has been used to make ceramic substrates impregnated by diamond grains size 8/16  $\mu\text{m}$  gradually from 0 to 66 weight %. Diamond films were deposited on the surface with maximum diamond grains concentration. To minimize the internal residual stress in multilayered diamond containing composites the theoretical calculations were fulfilled. Calculation model predicts an optimal amount of layers with different diamond concentration. This model was used to define the amount of layers in two composites produced by SHS. The number of layers was 5 in the case of ceramic matrix on the base of ( $TiB_2+TiSi_2+Si$ ) system with diamond concentration on the surface equal to 44% and 7 layers in the case of ( $Ti_3SiC_2+TiC+TiSi_2$ ) system with diamond concentration – 66%. Microstructure and phase state of these SHS- compositions were investigated.

The experiments on diamond film deposition were carried out on a microwave plasma chemical reactor using methane-hydrogen gas mixtures with  $CH_4$  concentration of 3%. The kinetic of deposition process was studied on FGM – samples 10x10 mm and 4.5 mm thick. Diamond coating with the thickness 85  $\mu\text{m}$  was deposited at the rate of about 3.5  $\mu\text{m}/\text{hour}$ . SEM, X-ray diffraction and microRaman spectroscopy were used for samples analysis. A compressive strength with level of the order of 1 GPa was established within the diamond films. The results of this work show advantages of SHS - diamond containing FGM substrates for deposition of highly adherent diamond coatings.

**P-2-115: Effect of Mechanical Activation on Phase and Structural Formation in SHS of Niobium Silicides**

*O.A. Shkoda, O.G. Terekhova, V.I. Itin, Yu.M. Maksimov, L.D. Chaluh*

*Department of Structural Macrokinetics of Tomsk Scientific Center of Siberian Branch of Russian Academy of Sciences, Tomsk, 634021 Russia*

Results of investigation of effect of mechanical activation (MA) of starting components on the structure and phase composition of niobium silicides, obtained by SHS are presented. It was shown, that the obtaining either multi-phase or one-phase product is possible in dependence on Nb and Si relation and MA duration. Calculations, made according to Sherrer method, showed, that nanostructural states of components and nucleus of niobium silicides phases, being obtained in MA, preserve after SHS, measurements of maximum temperature showed, that silicides synthesis proceeds through liquid phase formation. Changes in MA time dependent morphology of particles were shown with the use of raster electron microscopy.

**P-2-209: Electrical Resistance and Thermal Conductivity of Powder Mixtures on Titanium Base for Self-Propagated High-Temperature**

*A.N. Emelyanov, V.M. Shkiro, A.S. Rogachev*

*Institute of Structural Macrokinetics and Materials Science of RAS*

*142432 Chernogolovka, Moscow Region, Russia*

Lately appeared works on gasless combustion wave microstructure study demonstrate the existence of strong temperature inhomogeneities on microscopic level. These inhomogeneities, corresponding to metal reagent particle size, are the result of high thermal resistance of interparticle contacts (i.g. thermal conduction of the particle itself is much higher than that of inter particle contact). The consequence of heat microinhomogeneity is a possibility of superadiabatic self-heating in the narrow combustion wave band and it has a fundamental effect upon the temperature regime of the synthesis. The appearance of the relay-race regime of combustion can be considered as another consequence of heat microinhomogeneities, when the front propagation occurs as the series of microscopic flashes, in which one or several particles react. In order to understand these phenomena mechanism, to determine their existence area and to learn their controlling for materials synthesis purposes, it's necessary to investigate the contacts between the particles and to determine the role of contact thermal resistances in the gasless combustion mechanism on the basis of electro- and thermal conductivity of powder mixtures measurements.

Electrical and thermal conductivities of powder titanium (PTS) and spherical titanium powders from 0.2 till 1.2 mm measurements were carried out in this work. Thermal conductivity evaluation of contact in powder titanium was conducted as well. Its value is  $\sim 10^{-5}$  W/mK. The thin layer with low thermal and electrical conductivity, existing upon surface of titanium particles, is thus remained in blocks, compacted out of powders up to 80-90 % relative density. It result in the fact that the contact area thermal conductivity between the particles is some orders lower than that of the metallic particles themselves. The great difference in thermal conductivity of particles and inter particle contacts results in heat microheterogeneity of combustion wave (SHS) and the origin of relay-race regimes of solid flame front propagation.

This work is carried out due to RFBR support, grants No. 99-03-32392 and 00-15-97370.

**P-2-48: The Experimental Study of the Ionization Processes in the SHS wave**

*O.K. Kamynina<sup>1</sup>, N.I. Kidin<sup>2</sup>, V.A. Kudryashov<sup>1</sup>, A.S. Rogachev<sup>1</sup>, L.M. Umarov<sup>1</sup>*

*<sup>1</sup>Institute of Structural Macrokinetics and Materials Science*

*Russian Academy of Sciences, Chernogolovka, Moscow region, 142432 Russia*

*<sup>2</sup>Institute for Problems in Mechanics, Russian Academy of Sciences Vernadsky Ave, 101, bl.1, Moscow, 117526 Russia*

The charges particles formed in the gas phase of the combustion wave of the  $Ti_5Si_3$  system were experimentally studied for elucidation of the reaction mechanism and the kinetics of heterogeneous combustion. To gain the purpose two complementary methods were used: (1) the method of

Langmuir probe for determination the reacting particle charge and concentration, (2) the spectral method for determination of the atomic composition of the electrically active particles. The experimental data obtained by Langmuir probe method showed that near the reaction zone of the combustion wave the positive and negative charge carriers were formed. Their concentration was by 1-2 orders higher than both the equilibrium thermal ionization and the ionization due to thermal emission current from the titanium surface at the combustion temperatures. In turn, the optical measurements allowed a number of suppositions to be made concerning the nature of the registered charges particles in the combustion wave. Combination of the spectral and probe methods allowed obtaining of relatively complete illustration of the ionization in the combustion wave.

The present study has been partially supported by Russian Foundation of Basic Research (Grant №98-03-32147a).

#### **P-2-97: Extrusion-Induced Mechanical Activation of Al + NiO Powders and Subsequent Reaction in the Thermal Explosion Mode**

*D. Vrel<sup>1,2</sup>, P. Langlois<sup>1</sup>*

<sup>1</sup>*CNRS – LIMHP, 99 avenue J.-B. Clément, 93430 Villetaneuse, FRANCE*

<sup>2</sup>*CNRS – GFA, GDR 2391, J.-C. Nipce, LRRS, 9 av. A. Savary, B.P. 47870, 21078 Dijon Cedex, FRANCE*

Mechanically Activated Self-Propagating High-Temperature Synthesis (MASHS) has been the subject of many interesting studies, especially in the domain of nanomaterials synthesis. Recently, a new way for densifying such materials has been patented in the US. But the general understanding of such a process proves to be difficult since SHS is intrinsically complex, as is mechanical activation. In order to understand how mechanical activation operates, we can roughly distinguish between size-related or mechanics-related effects, the first being due to the small size of the particles (<100 nm), and the second to the treatment itself, which can induce an unusual mechanical state (high dislocation density, high-strain state, lack of an oxide layer at the metal surface). We therefore tried to separate size-effects from mechanics-effects, by using extrusion in order to create mechanical activation without reducing (at least not significantly) the particle size. Densification of SHS-produced ceramics itself constitutes a difficult task, since the as-produced samples generally have a porosity close to 50%, i.e. close to the initial powders density, and since high-density powder mixtures can even produce a final sample with a greater porosity than in the starting conditions. It has been suggested that this porosity was due to a particular chemical path. If the oxide layer were to be removed, and thus the chemical path changed, it should then be possible to produce a sample with no increase of the overall porosity. Samples of Al and NiO powders were mixed with the 2-3 and the 5-3 stoichiometry (2 Al + 3 NiO → Al<sub>2</sub>O<sub>3</sub> + 3Ni; 5 Al + 3 NiO → Al<sub>2</sub>O<sub>3</sub> + 3NiAl), isostatically compacted at 600 MPa, machined into a 6 mm diameter rod and then inserted in a copper tube of 6 mm inner diameter and 8 mm external diameter. These samples were then hydrostatically cold-extruded through a 4.5 mm, tungsten carbide die. After recovery, high intensity current was set through the sample (up to 300 A), which would heat the sample up to the point where the reaction would start. Effects of current, time of heating will be presented, and results obtained by SEM, XRD, will be shown and discussed.

#### **P-2-194: Fabrication of Symmetrically Compositional FGM with SHS/Pseudo HIP Technology**

*Chang-Chun Ge<sup>1</sup>, Wei-Ping Shen<sup>1</sup>, Wen-Bin Cao<sup>1</sup>,*

*A.G. Merzhanov<sup>2</sup>, A.S. Rogachev<sup>2</sup>, H.E. Grigoryan<sup>2</sup>, A.E. Sytschev<sup>2</sup>*

<sup>1</sup>*Laboratory of Special Ceramics and Powder Metallurgy*

*University of Science and Technology, Beijing, China*

<sup>2</sup>*ISMAN, Russian Academy of Sciences, Chernogolovka, Moscow, 142432 Russia*

Symmetrically compositional FGM (SCFGM) is a special kind of FGM, which has symmetrical composition and structure distribution. The design of SCFGM is based on the compressive stresses,

which are developed upon cooling due to the relatively higher expansion coefficient in the inner layers and enhance the strength and fracture toughness of the surface layers. SHS in combination with pseudo-Hot-Isostatic Pressing (HIP) is an advanced technology for making FGM. It can be realized on conventional hydraulic presses instead of expensive HIP facilities. Though many SHS FGM have been reported in literatures, yet the features of combustion wave propagation in making SHS FGM have not been reported by other authors. In this paper, the features of combustion synthesis in bi-layered and multi-layered SCFGM of (Ti-2B-Me) and (3Ti-2BN-Me) systems were investigated. On the basis of this investigation, densified SCFGM of 3Ti-2BN-Me system has been fabricated and its composition distribution, XRD patterns and gradation of hardness are reported.

### **P-2-37: Highly Efficient Corrosion-Resistant SHS Filters**

*I.P. Borovinskaya, A.G. Merzhanov, V.I. Uvarov*

*Institute of Structural Macrokinetics and Materials Science RAS, Chernogolovka 142432  
Russia*

A fundamentally novel method of producing advanced porous materials for filtering elements, based on refractory inorganic compounds (carbides, nitrides and oxides), has been developed. Porous materials produced by SHS method are alternative to the sintered. Structure of the filters can be both, homogeneous and graded. The graded SHS filters have got a selective titanium carbide layer of 100  $\mu\text{m}$  in thickness with pores of 0.1–1  $\mu\text{m}$  in size and a firm carbide substrate of 5 mm in thickness with pores of  $\sim 15 \mu\text{m}$  in size. Their basic characteristics (filtration properties, sorption ability, and regeneration ability) are perfect. Bactericidal properties, corrosion resistance and thermal stability of SHS filters are high. Water pollution with salts of heavy metals (salts of uranium, lead, iron and cobalt among them) and with toxic light elements of organic compounds reduces. The degree of water hardness decreases up to 30 %. SHS filters (pipes and vessels) up to 1000 mm in length have been developed. Capacity of SHS filters with disks of 80 mm in diameter and 5 mm in thickness (for domestic and work buildings, cottages) is 250 L/h. Capacity of an industrial plant made of 6 changeable filters-vessels is 10000 L/h at 1  $\text{kg}/\text{cm}^2$  pressure gradient. It stands working pressure up to 6  $\text{kg}/\text{cm}^2$ . The filters were used in vodka distillery “Topaz”. When set up at the final purification stage, they were found effective to purify vodka from toxic metal ions: Cu, Sr, Zn, Si, Ca, Na, and some harmful organic compounds. In the Institute of physicochemical medicine, investigations on blood preservation by its filtration and plasma saturation were carried out. In addition, laboratory test on sterility was performed. It was found that filtration through TiC-filter reduces concentration of bacteria (*staphylococcus epidermidis*) in the dredge a hundred times. SHS-filters excel Millipore’s, Sartorius’s, Seitz’s, and Whatmen’s filters in their characteristics. Comparable analysis of prices of modern filters demonstrates the advantages of SHS filters. Reusability of the filters after regeneration, which is impossible for many kinds of filters produced by conventional methods, is especially valuable.

This work is supported by Russian Foundation for Basic Research, grant RFBR 00-15-99054.

### **P-1-191: Hydrodynamics and Heat Change at the Melt Spreading Along the Substrate**

**Surface in SHS Surfacing**

*A.V. Yukhvid, L.S. Stelmakh*

*Institute of Structural Macrokinetics and Materials Science*

*Russian Academy of Sciences, Chernogolovka, 142432 Russia*

The role of spreading during SHS surfacing of the protective coatings has been investigated theoretically and experimentally. The case, when spreading of large drops is forced by the effect of gravity and the interface forces are low, is considered. Analytical and numeric solutions of the problem have shown that the ratio of the specific times of cooling and spreading is the main parameter, which determines the dynamics and the final characteristics of spreading.

It has been shown that the process of spreading is most strongly affected by the initial melt mass and drop size, the activation energy of viscosity, and gravitation (microgravitation and overload)

within these specific times. The experimental research into SHS surfacing has confirmed the theoretical data.

### **P-2-117: Investigation and Properties of Niobium Nitrides Obtained from SHS Nitrided Ferroniobium**

*L.N. Chuhlomina, M.Kh. Ziatdinov, Yu.M. Maksimov*

*Department of Structural Macrokinetics of the Tomsk Scientific Center of  
Siberian Branch of Russian Academy of Sciences, Tomsk, 634021 Russia*

The process of obtaining of niobium nitride from ferroniobium by means of its nitriding with SHS and subsequent extraction of niobium nitride through acid enrichment are investigated in the work. Nitrogen containing ferroalloys, obtained with SHS have high nitrogen content and composition structure. Therefore, their use as starting compositions during acid enrichment is prospective one. The nitriding of ferroniobium was conducted in combustion at nitrogen pressure from 0,2 to 8 MPa, relative density of samples varied in the limits. The synthesis product was subjected to chemical and X-ray phase analysis after the combustion. The depth of transformation becomes close to 1 with pressure increase up to 8 MPa. The product, being formed in combustion has two-phase structure and consists of  $\delta$ -niobium mononitride and  $\alpha$ -iron. According to X-ray phase analysis data, products of ferroniobium nitriding at low pressure contained the known nitride phases:  $\gamma$ -Nb<sub>4</sub>N<sub>3</sub>,  $\beta$ -Nb<sub>2</sub>N,  $\delta$ -NbN and  $\beta$ -Fe. The portion of niobium mononitride increases with the increase in pressure and two-phase composite Fe-NbN alloy is formed over 2 MPa. Acid enrichment of nitrided ferroniobium is conducted in special device, equipped with thermostat and mixer, in solutions of hydrochloric acid. In this case, the iron passes into the solution, and niobium mononitride, stable in hydrochloric acid solutions, is extracted as dispersed powder. It was stated that the degree of acid enrichment depends on acid concentration, its temperature, size of particles of nitrided ferroniobium. In this case the dissolution of composite alloy of niobium nitride-iron proceeds in two stages. At the first stage the rate of process depends on acid concentration and its temperature. At the second stage the rate is possibly limited by acid supply through micropores of the composition to residual iron or by diffusion rate of iron from particle volume to interface. The value of seeming energy of activation process of acid enrichment was determined, its value changes from 8 to 2-3 KJ/mol. According to the chemical analysis data, niobium mononitride, being extracted ( $\delta$ -NbN cub.) contains of 0.5 mass % of iron. Its specific surface was determined by BET method. Oxidation resistance of SHS niobium nitride was investigated with differential thermal analysis. Chemical resistance of extracted niobium mononitride was investigated with gravimetric method.

### **P-2-27: Investigation of Self-Propagating High-Temperature Synthesis of Materials with Micaceous Structure -Fluorophlogopites**

*V.E. Loryan, V.V. Tkach*

*Institute of Structural Macrokinetics and Materials Science, RAS, Chernogolovka,  
Moscow 142432, Russia*

It is well known that items obtained from melted mica-crystalline materials are successfully used as corrosion-resistant refractories reliably operating in the medium of aggressive moving melts of nonferrous metals (aluminum, zinc) at temperatures of up to 1100°C. Conventionally, a cast mica-crystalline material is obtained by its crystallization from the melt with the help of the method of igneous synthesis at T=1500°C. A green mixture close to the required fluorophlogopite in its composition is melted in arc or induction furnaces but it is connected with significant power consumption. An alternative method for obtaining synthetic mica can be the SHS method which allows one to carry out the synthesis in the open air in the case of a proper composition of the green mixture and does not require high power consumption and expensive equipment. Also, the homovalence and heterovalence isomorphism observed in micas makes it possible to vary widely

qualitative and quantitative composition of a combustible component in the green mixture during the SHS. Besides, properties of the micas obtained can be regulated in the known range.

The paper describes the SHS of the following phlogopites:  $\text{NaMg}_3[\text{Si}_3\text{AlO}_{10}]\text{F}_2$  and  $\text{KMg}_3[\text{Si}_3\text{AlO}_{10}]\text{F}_2$ . A mixture of oxides (silicon dioxide, magnesium oxide, aluminum oxide), metals (magnesium, aluminum), oxygen, potassium, sodium, and fluorine-containing components were used as a green mixture. Changes in the green mixture composition allowed us to regulate the compound aggregate state in the combustion wave in the range from a melt to an ordinary cake. Items of fluorophlogopite were synthesized in the form of cups ( $d=40$  mm,  $h=100$  mm). Our analysis of the samples synthesized has proved that the phlogopites produced by the SHS method are characterized by a finer structure in comparison with those obtained by a conventional method. This work is supported by Russian Foundation for Basic Research, grant RFBR 00-15-99054.

#### **P-1-8: Investigation of SHS Fine Thermal Structure by High-Speed Digital Infra-Red Imaging Method**

*V.V. Evtigneev, P.Y. Gulyaev, V.I. Yakovlev, Polzunov Altai State Technical University  
Str. Lenina 46, Barnaul 656099 Russia, Fax: (8-385-2) 367864, 368463*

Nowadays available methods of condensed systems combustion processes registration are mainly based on traditional thermocouple methods. However, modern level of combustion mechanisms understanding requires more modern registration methods implementation, giving the possibility to analyze fine structure of combustion both in front mode and thermal explosion mode. That is why the development of the methods of high-speed pyrometry, high-speed digital imaging, responsive processes, spectrum express-analysis of thermal radiation is actual both for theory and practice.

According to the stated-above the work investigates technologically significant binary systems Ni-Al, Ti-Al by high-speed video recording both in layer-by-layer combustion mode and thermal explosion mode. The lack of sluggishness and contact, high responsiveness characterizing this method, allowed to determine complicated structure of thermogram (using light microscope) in Ni-Al system determined by the processes of melting, dissolution, phase formation, and corresponding on the whole to equilibrium diagram of the system. The investigation of heating up dynamics in Ti-Al system in the mode of thermal explosion allowed to come to the conclusion that homogenous in the volume heating up in the indicated system has never been realized, but place ignition happens in the separate parts of the mixture. The method of high-speed video recording allowed to determine temperature profiles dynamics and shape, to calculate effective speed of place combustion front and reveal the laws of its propagation.

The investigation results open practical possibilities of diagnostic, control, optimization of technological conditions of self-propagating high temperature synthesis.

#### **P-1-84: Investigation of Spark Ignition of the Gas-Suspended Solid Fuel via the Model of Spot Ignition**

*B.S. Seplyarskii, T.P. Ivleva  
Institute of Structural Macrokinetics and Materials Science  
Russian Academy of Sciences, Chernogolovka, 142 432 Russia*

In the present study the process of ignition of a gaseous suspension with a spark discharge is described with the use of a model of spot ignition. Such an approach allows retaining of the specific features of spark ignition, considerable simplification of the calculation manipulations and, in some cases, the problem solution in the form of simple analytical dependencies of the critical size of the spot on the major parameters of the process. The following model process is considered. The still particles of the radius  $R$  are uniformly distributed over the gas containing an oxidant. At  $t=0$ , the energy is instantaneously released in some part of the suspension volume. Since the volume portion of the particles is low, it is assumed that the energy is solely consumed by the gas heating. Therefore, the initial distribution of the gas temperature  $T_g$  is randomly described by the constant function  $T_g = T_{ig}$  in the spot ( $|x| < r_h$ ) and  $T_g = T_0$  at  $|x| > r_h$  and the particle temperature  $T_p$

is equal to  $T_0$ . The process is described by a two-temperature mathematical model suggesting that the particle and gas temperatures can be different. The study was aimed at determination of such  $r_h = r_{cr}$  value as a function of the governing parameters that at  $r_h > r_{cr}$  the spot ignition can be expected, while at  $r_h < r_{cr}$  the initial temperature perturbation will vanish, *i.e.* the temperature distribution in the gas suspension will become uniform,  $T_p = T_g = T_0$ . The physical cause of the existence of the critical conditions is competition of two processes of the spot heating owing to the chemical reaction and its cooling initiated by the thermal conductivity. At high values of the heat exchange coefficient  $\alpha$ , an analytical expression for  $r_{cr}$  calculation was obtained. For low values of the heat exchange coefficient  $\alpha$ , the value of  $r_{cr}$  was derived numerically. As shown by the results of numeric calculations, the formula gave the correct value of  $r_{cr}$  (the error did not exceed 15% in the region of high coefficients of heat exchange  $\alpha$ , the one-temperature model). The  $r_{cr}$  value increased with  $t_h \geq 1/\alpha$  (diminishing of  $\alpha$  and increasing of  $R_0$ ). However, the increase was not significant, *i.e.* the ratio  $r_{cr}(\alpha)/r_{cr}(\alpha \rightarrow \infty) < 1.5$  retained within the whole range of the governing parameters variation. A few-fold increase in the ignition time  $t_{ig}$  was observed at extension of the heating time  $t_h$ . Analysis of the results of the present study led to the conclusion that within the frames of the proposed model, at the equal particle mass contained in the unit of the gaseous suspension volume the minimum energy of ignition was weakly dependent on the particle size.

The study was supported by RFBR (Grant 00-03-32034) and INTAS -ESA (Grant 99-0138).

## P-2-205: Joining SiC-Based Materials by SHS

*Galina Xanthopoulou, George Vekinis*

*Institute of Materials Science, NCSR "Demokritos", Greece – 15310*

*E-mail: [gxantho@ims.demokritos.gr](mailto:gxantho@ims.demokritos.gr)*

SiC and SiC/SiC composites are being developed for a number of extreme applications, such as elements of jet engine exhaust flumes and the plasma-facing blanket of the thermonuclear fusion reactor. In all cases, an important consideration is the development of an efficient and easy-to-use joining method. The main problem is the high sensitivity of SiC to high temperatures over extended periods when it can oxidize degrading its properties. Special brazing alloys that have been developed present difficulties in being applied over relatively large areas.

The SHS method offers advantages by being able to be applied over relatively large areas in the form of thin layers and the very short time needed for completion. We have considered a number of SHS systems as possible candidates for joining SiC, some of which are presented here.

## P-2-133: Magnesium-Reduced Obtaining of Niobium Powders from Niobium Pentoxide by SHS Mode

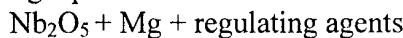
*V.I. Vershinnikov, I.P. Borovinskaya*

*Institute of Structural Macrokinetics and Materials Science*

*Russian Academy of Sciences, Chernogolovka 142432, Russia*

Niobium is characterized by high melting point, excellent machinability, corrosion resistance, and quite low thermal neutrons capture cross section. It is used in chemical machine building, electrovacuum engineering, production of heat-resistant alloys and alloyed steels.

The paper investigates the process of obtaining a niobium powder from its pentoxide by the SHS method according to the following equation:



The mixtures burn in a self-oscillating mode. The samples of a bulk density were used in paper cups. The sample diameter was changed from 25 up to 65 mm, their height was 40 mm. The burning velocity and rate were determined using a tungsten-rhenium thermocouple (W-Re 5/20) of 100  $\mu\text{m}$  in thickness. We studied influence of magnesium (Mg), magnesia (MgO), calcium hydride ( $\text{CaH}_2$ ), calcium peroxide ( $\text{CaO}_2$ ), magnesium perchlorate ( $\text{Mg}(\text{ClO}_4)_2$ ) content in a green mixture on combustion parameters ( $T_c$ ,  $U$ ,  $\Delta m$ ,  $\Delta h$ ), phase composition, particle morphology and size of the

niobium powder obtained. In the case of 10 % magnesium excess in the green mixture we obtained niobium powder with minimum content of impurities.

This work is supported by Russian Foundation for Basic Research, grant RFBR 00-15-99054. .

#### **P-1-165: Microstructure of SHS-Derived Sialons**

*Dariusz Kata, Jerzy Lis*

*Faculty of Materials Science and Ceramics, University of Mining and Metallurgy  
30-065, Cracow, Poland*

Sialons and related systems are being extensively explored for their thermal, mechanical, and chemical properties. These depends on the microstructure nature. Different preparation technique; the conventional on one side and the SHS on the other side can lead to the differences in the sintering process and consequently to preparation different microstructures. An attention was focused to analyze the microstructures of sialon materials produced from SHS derived powders. The  $\beta$ -sialon has the silicon nitride hexagonal structure with a homogeneity range  $Si_{6-z}Al_zO_zN_{8-z}$  where  $z$  reaches a maximum of about 4.2. Three types of  $\beta$ -sialon powders (i)  $z = 0.5$  (ii)  $z = 1$  (iii)  $z = 3$  were prepared by combustion and next carefully examined by SEM and XRD technique with emphasis placed on investigation reaction route. Combustion products were next densified by pressureless sintering in a graphite furnace for 2 h at different temperatures ranges from 1620 to 1720°C under nitrogen ambient pressure. Chemical etching was carried out prior to SEM observation to reveal the microstructure details. Formative grains diameters ( $d_{av}$ ) as well as grains elongation factor ( $\beta$ ) and grains boundaries factor ( $\alpha$ ), were determined. Basis on these analysis it was found that the sialon polycrystals fabricated from the SHS-derived powders exhibit isotropic microstructure. There is clear tendency toward the grains growth as amount of Al and O elements in sialon structure increases but in opposite to the typical silicon nitride based material, the elongation of grains does not significant occur. This hypothesis was proved mathematically by variance method. Finally, the hardness fracture toughness (*Vickers indentation method*) and stiffness (*ultrasonic method*) were evaluated. Wear resistance tests documented a very good material resistance much higher than for steel tools and it can be comparable to the best boron carbide ceramic. A possibility for utilization of sialon ceramic as advanced cutting tools and wear resistance pomp sealing is discussed.

#### **P-1-184: Modeling an Emergency Situation in Atomic Reactor by SHS**

*N.Uu. Medvedeva<sup>1</sup>, V.I. Yukhvid<sup>2</sup>, V.N. Sanin<sup>2</sup>, S.V. Rodinov<sup>1</sup>*

*<sup>1</sup>Research Center on Safety of Nuclear Stations, Elektrogorsk, Moscow Region, 142530, Russia*

*<sup>2</sup>Institute of Structural Macrokinetics and Materials Science  
Russian Academy of Sciences, Chernogolovka, 142432 Russia*

The research is directed on modeling of an emergency in nuclear reactor such type as RMBK. An emergency situation arises in case of absence of thermal balance between heat emission and heat lose in working cells of the reactor. The new experimental stand was created. Experimental modelling of the emergency heating in an individual reactor cell with the help highly exothermic thermit mixture is simulated in the stand. The carried out researches have shown that temperature and heating rate of the reactor cell can be variated by mixture composition of the thermit and geometrical characteristics of thermit charge. The conditions at which the working cell of the experimental stand is heated to critical temperature necessary for destruction of Zr pipe are determined.

## P-1-85: Modeling of the Electrothermal Explosion in the Layered Ni-Al System

V.A. Gorelski<sup>1</sup>, A.Yu. Smolin<sup>2</sup>, A.S. Shtenberg<sup>3</sup>

<sup>1</sup>Tomsk State University, Tomsk (Russia)

<sup>2</sup>Institute of Strength Physics and Materials Science of Siberian Division RAS, Tomsk, Russia

<sup>3</sup>Semenov Institute of Chemical Physics of RAS, Moscow Russia

Study of kinetics and macrokinetics of rapid and high-temperature reactions in heterogeneous condensed systems enabling gasless combustion is interesting not only theoretically but also important from practical point of view. It is obviously that the laws of such processes govern not only velocity and limits of combustion of corresponding mixtures, but they influence on depth of reactions and thus on the quality of the SHS products obtained. It is known, that the study of mechanisms of gasless combustion of a range of condensed systems including gasless SHS mixtures and multilayered samples has been restrained for a long time due to absence of corresponding methods. In the last few years the method of electrothermal explosion (ETE) is widely used for these purposes. The essence of the ETE-method consists of the rapid Joule heating of the green mixture followed by switching off the electrical current and continuos registration of increase of the sample temperature. Due to high rate of self-heating this temperature increase occurs in condition close to adiabatic one. Computations of kinetic parameters are correct if the part of a sample where the temperature is measured is heated without considerable non-homogeneity of temperature field, i.e. there is so called «homogeneous heating». Meanwhile the authors of the ETE-method have noted that depending on conditions of Joule heating (perfection of the contact between the electrodes and surface of the sample, the ratio of the sample length and diameter and so on) ETE may occurs as spatially inhomogeneous process and even as a combustion wave. In this connection for correct estimation of ETE conditions it is necessary to carry out mathematical modeling of time-dependent ETE process in two-dimensional statement. This problem is considered in this paper. The mathematical model includes the equation of energy conservation and the equation for chemical reaction rate. According to the experimental ETE data the rate of the first and main stage of the reaction for Ni-Al multilayered sample is assumed to be limited by dissolution of nickel in melted aluminum. The temperature at the faces of the cylinder is assumed to be constant and equal to the temperature of electrodes, heat loss at the lateral surface of the cylinder is described by the Stefan-Boltzmann law. Process of melting of aluminum during heating is described with using of the phase diagram. The problem is solved numerically using the finite element method. The intensity of Joule heating and the parameter of heat exchange at the lateral surface are varied in wide range. The dependence of the critical conditions of ignition on the varied parameters is investigated. The distributions of temperature in the cylinder at different times are presented. The computations show that when the intensity of Joule heating is low the reaction is initiated at the central part of the axis of the cylinder and propagates to the boundaries. When the intensity of heating is high the electrothermal explosion of Semenov regime takes place. In the intermediate region of the heating intensity a propagation of the wave with super high velocity takes place.

## P-1-70: On the Mechanisms of Chromium Carbides Synthesis by Activated SHS

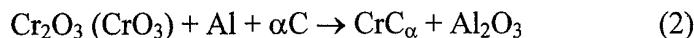
Kh.V. Manukyan, S.L. Kharatyan, H.H. Nersisyan

Nalbandyan Institute of Chemical Physics NAS of Armenia, 375044, Yerevan, Republic of Armenia

The carbides of chromium are widely used in the industry as hard, wear-resistant and stable to aggressive environment materials. Among the methods of synthesis of these substances a special interest presents SH-synthesis from the elements. However, unlike many reactions of carbidization, the reaction



has rather low heat efficiency and does not provide the self-sustaining mode of the process. Therefore SH-synthesis of chromium carbides was realized from chromium oxides using high-exothermic reaction



However the carbides obtained by this reaction have not got high yield and purity. Therefore the problem of SH-synthesis of pure single-phase chromium carbides with the high yield remains urgent and not solved till now.

In the present work the conditions for synthesis of chromium carbides by the reaction (1) under the activated combustion mode were investigated. Powdered polytetrafluoroethylene (teflon) and high-exothermic mixture of magnesium with teflon were used as activate additives.

Researches carried out have shown that both additives are capable to activate the combustion process. In both cases a steady combustion mode is registered with the velocity of wave propagation about 0.05-0.3 cm/s. It is established that depending on  $\alpha$  and the type of additive used the combustion temperature changes in the interval 1300-1800K. Optimum conditions for synthesis of single-phase  $\text{Cr}_3\text{C}_2$  and  $\text{Cr}_7\text{C}_3$  carbides depending on  $\alpha$  and amount of teflon in initial mixture are determined.

According to microstructural analysis data, when using teflon as the additive, the carbide grains have the size less than 1.0  $\mu\text{m}$ , that is much less than the sizes of initial chromium (5-10  $\mu\text{m}$ ). In the case of the magnesium-teflon additive the sizes of initial chromium and carbide grains obtained are practically the same.

It is established that depending on the type of the additive two mechanisms of activation are realized: thermokinetic (when teflon is used) and thermal (when the magnesium-teflon mixture is used). It is revealed that at thermokinetic activation the gas-transport mechanism of chromium carbidization by means of intermediate high-volatile fluorides ( $\text{CrF}_2$ ,  $\text{CrF}_3$ , etc.) is realized. At thermal activation the fluorine is mainly bound as  $\text{MgF}_2$ , and the formation of carbides proceeds by the solid-phase mechanism, i.e. the diffusion of carbon into the chromium crystal lattice through the product layer.

## **P-2-26: On Melting at SHS of Nitride Ceramics at High Nitrogen Pressure**

*V.E. Loryan, I.P. Borovinskaya*

*Institute of Structural Macrokinetics and Materials Science, RAS*

*Chernogolovka, Moscow 142432, Russia*

Possible application of high nitrogen pressure for obtaining nitrides by the SHS method (such pressure suppresses dissociation of products in the combustion wave) allows one to establish one of the possible combustion mechanisms. It is a combustion mechanism with a change in a compound aggregate state, in particular, melting of compounds in the combustion wave.

The paper shows that during aluminum nitriding at  $P_N=300$  MPa melted aluminum nitride is obtained. In this case the combustion temperature and the melting point of aluminum nitride are equal to  $\sim 2500^\circ\text{C}$ .

It is also shown that melted aluminum nitride can be obtained at nitrogen pressure ranging from 150 to 300 MPa and ambient temperature being about  $3000^\circ\text{C}$ .

At  $P_N=150-200$  MPa and  $T_{\text{amb.}}=3000^\circ\text{C}$  it is possible to obtain melted boron nitride.

This work is supported by Russian Foundation for Basic Research, grant RFBR 00-15-99054.

## **P-1-68: On Modeling of Ions Dynamics during SHS-Processes in Oxide Systems**

*V. A. Fedotov, Yu. G. Morozov, M. V. Kuznetsov*

*Institute of Structural Macrokinetics and Materials Science*

*Russian Academy of Sciences, 142432, Chernogolovka, Russia*

Despite of intensive investigations, the role of charged particles in the mechanism of combustion wave propagation in heterogeneous media still does not establish. The systematic dynamic model

operating only the reliably known physical laws and physicochemical properties, can give a clue to understanding of non-explained effects which take place in SHS-reactions, and also to forecast an influence of external actions (such as electrical and electromagnetic fields) on SHS-processes. For oxide systems, in which the electrical effects during SHS-processes are stipulated in the greater degree by an ionic transport, such a model has been developed. In this model both heat effects in separate zones of SHS-process and diffusion electromigration are taken into consideration simultaneously. This multi-compartment model is tested on the experimental data obtained from the dynamic ionography for SHS-system  $\text{BaO}+\text{CrO}_3$ , and answers questions like "What if..." for different types of real and virtual actions on SHS-reaction. The model can be debugged on other oxide systems and distributed on a wide area of typical SHS-processes.

This work is supported by Russian Foundation for Basic Research, grants RFBR 01-02-16126a, 01-03-32863a, 00-15-99054.

#### **P-2-208: On Possible Synthesis of Single-Phase Tungsten Monocarbide from $\text{WO}_3$ by SHS Method WC-Based Material**

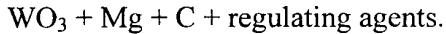
*V.I. Vershinnikov, I.P. Borovinskaya*

*Institute of Structural Macrokinetics and Materials Science*

*Russian Academy of Sciences, Chernogolovka, 142432 Russia*

Tungsten carbide WC is characterized by high hardness, wear and heat resistance. The most efficient hard alloys are being developed on the base of tungsten carbide. Such alloys contain WC and cobalt. Some of them can also include titanium, tantalum, and niobium carbides.

The paper studies the SHS production of tungsten carbide powders from its trioxide by the following reaction:



The samples of bulk density in paper cups were burnt under the self-oscillating mode.

The sample diameter was ranged from 20 up to 50 mm, its height was 40 mm. When the samples were burnt in the reactor, their diameter was changed from 10 to 17 cm, their mass being 3-30 kg. The burning rate and temperature were determined using a tungsten-rhenium thermocouple WRe 5/20 of 100  $\mu\text{m}$  in thickness.

We studied the influence of magnesium, magnesia ( $\text{MgO}$ ), carbon black, polyethylene, ammonium chloride contents in the green mixture and an initial pressure on the combustion parameters ( $T_c$ ,  $U$ ,  $\Delta m$ ,  $\Delta h$ ), phase composition, morphology, and particle size of tungsten carbide powder. We determined the optimum conditions for synthesizing tungsten monocarbide with its particle size being 0.1-0.15  $\mu\text{m}$  (50 % being less than 1  $\mu\text{m}$ ). Free carbon content was less than 0.04 % at  $C_{\text{total}}=6.2\%$ , oxygen content changed from 0.06 up to 0.02 %. We also sintered the material VK - 6 s.f., WC + 6 % Co from the obtained tungsten carbide. The alloy characteristics:

Specific weight, g/cm <sup>3</sup>	- 14.9
Hardness, HRA	- 91
Bending strength, kgf/mm <sup>2</sup>	- 170
Stability factor ( $K_{\text{st}}$ )	- 1.4

Cutting properties of the alloys became 4 times higher than those of the standard one.

#### **P-1-30: On a Theory of "Ignition" of Catalytic Combustion Reaction by Laser Beam**

*V. Barelko, K. Pribitkova*

*Institute of Problems of Chemical Physics RAS, Chernogolovka*

It was carried out a theoretical analysis of threshold phenomena of excitation (ignition) of exothermic heterogeneous catalytic reactions by spatially local thermal disturbance from radiant source (laser beam). The study was fulfilled on a base of a one-dimension model for industrial important reactions of catalytic combustion. The received results may be used for development of ignition problem in wide raw of different reactions in solids and on its surface.

### **P-1-54: Patenting in the Field of SHS**

*T.V. Bavina<sup>1</sup>, L.V. Peresada<sup>1</sup>, O.N. Chernenko<sup>1</sup>, L.A. Yurkova<sup>2</sup>*

*<sup>1</sup>Institute of Structural Macrokinetics and Materials Science, Chernogolovka*

*Moscow Region, 142432 Russia; e-mail: [patent@ism.ac.ru](mailto:patent@ism.ac.ru)*

*<sup>2</sup>The Department of Structural Macrokinetics of  
Tomsk Scientific Centre SB RAS*

In this communication, we report on current situation in patenting recent innovations in Russia, the USA, and Japan as leading countries in the field of SHS research and development. Our analysis shows that the largest number of patents was taken in 1986-87, 1994, and 1999 in Japan; in 1990-91, 1994 and 1999 in the US; and 1993 and 1995 in Russia.

Over a period of 1970–2000, the dynamics of patenting was found to exhibit maxima and minima for each of the above countries. For instance, the pace of patenting in Russia was higher in 1993 and 1995. However, in past two years the pace of growth have become higher in the US and Japan. Our analysis shows the following trends. Methods for manufacturing porous materials and items, for immobilisation of highly radioactive nuclear wastes, and for fabrication of metals and powder materials are prevailing in Russia. Complex ceramics, cermets, functionally graded materials, and powder materials are the leading trends in the USA. In Japan, these are intermetallides, superabrasives, and ceramics.

In all of the countries under consideration, domestic applicants are predominant. Nevertheless, there is a trend for patenting in the US by foreign applicants from Russia, Japan, Germany, Canada, France, Taiwan, and Switzerland.

### **P-1-116: Possibility of Electrophysic SHS Phenomena Employment in High-Current Electronics**

*Yu.M. Maksimov<sup>1</sup>, A.I. Kirdyashkin<sup>1</sup>, V.S. Korogodov<sup>2</sup>, V.A. Polyakov<sup>2</sup>*

*<sup>1</sup>Department of Strucrural Macrokinetics of TSC SB RAS, Tomsk 63402, Russia*

*<sup>2</sup>Tomsk State University of Systems of Direct and Radioelectronic, Tomsk, 634050 Russia*

Self-propagating high-temperature synthesis is characterized by record high rate of dissipation of chemical energy in volume unit of combustion wave, reaching the value of  $10^{12}$  W/m<sup>3</sup>. Owing to considerable energy flows, SHS propagation is followed by the complex of unequilibrium electric effects, increased current of electrons emission of condensed substance of the combustion wave in particular.

On the sample of combustion of binary compounds Co-Al, Ni-Al, Ti-C it was shown that the density of emission current in vacuum interval achieves  $\sim 2 \cdot 10^5$  A/m<sup>2</sup> at accelerating strength of external field of  $\sim 4 \cdot 10^3$  W/m.

The aforementioned emission effect may be used as the switch in high current electronics. In external electric circuit, containing electromotive source, the SHS product, and anode electrode in vacuum of gas interval, the current being proportional to the emission on, will draw/ Current pulses of  $\sim 4 \cdot 10^3$  A and duration of  $10^{-2}$  sec at 0.5 level were obtained at combustion rate of  $\sim 10$  mm/sec.

### **P-2-199: Preparation LaCoO<sub>3</sub> Perovskite Oxide Using Field-Activated SHS**

*H. Wang, Z.Y. Fu, W.M. Wang, R.Z. Yuan, State Key Lab of Advanced Technology for  
Materials Synthesis and Processing, Wuhan University of Technology  
Wuhan 430070, P. R. China*

Perovskite-type metal oxides with the structure of  $ABO_3$  have attracted great attention due to their excellent electric, optical, magnetic and catalytic properties. Pure LaCoO<sub>3</sub> Perovskite Oxide was prepared by the field-activated SHS in air. Effects of combustion temperature and velocity on the magnitude of electric field were investigated. The mechanism of structural formation was also analyzed by combustion wave front quenching (CFQ) method. The structures and compositions of reaction products were characterized by scanning electron microscopy and X-ray diffraction. It is shown that the electric field has significant effect on SHS reaction process and reaction products.

#### **P-1-45: Regularities of Mechanical Activation Effects on SHS-Process Characteristics**

*V.V. Kurbatkina<sup>1</sup>, E.A. Levashov<sup>1</sup>, M.T. Trtanj<sup>2</sup>, M. Todorovich<sup>2</sup>*

<sup>1</sup>*SHS-Center of the Moscow Steel and Alloys Institute and the Institute of Structural Macrokinetics and Materials Science of RAS, Leninsky prospect, 4, 164, Moscow 119991, Russia*

*Phone: +(095) 230-4642, Fax: +(095) 236-5298*

<sup>2</sup>*Institute for Nuclear Science "VINCA", Belgrade, Yugoslavia*

Mechanical activation (MA) of initial powder reagents and their exothermic mixtures is one of effective ways of intensification of chemical reactions. Moreover MA in optimal regimes provides to realize the combustion process in low exothermic chemical reactions, which cannot be initiated in usual conditions at the room temperature. There are two mains MA effects on reaction mixture: accumulation of MA energy by initial charge and grinding of powders. The first one determines thermodynamic MA effect on combustion process and the second one – kinetic MA effect on combustion wave propagation. Relationship between those effects strongly depends on MA regimes and chemical composition of green mixture.

Effect of MA on macrokinetic characteristics of the combustion process, phase state, structure, and physical-mechanical properties of synthesized products in Ti-Si, Ti-B, Ti-Si-C, Ti-B-Si, Ti-B-C systems was studied in this work. Dependencies between specific surface of green mixtures, heat evolution and heat evolution rate of combustion processes of the different SHS- systems, on the one hand, and MA regimes, on the other hand, were established.

It was proposed the method of theoretical and experimental estimation of MA effect on an activation energy variation of the combustion process using high-speed calorimeter.

High quality porousless composite materials have been produced by force SHS-pressing technology using preliminary MA of initials reagents and their mixtures.

#### **P-1-49: Regularities of Self-Propagating High-Temperature Synthesis of AlN without Additives**

*V.V. Zakorzhevsky, I.P. Borovinskaya, N.V. Sachkova*

*ISMAN, Chernogolovka, Moscow 142432, Russia*

The present paper demonstrates some regularities of synthesizing aluminum nitride from the green mixture of Al+AlN without any gasifying additives. The influence of the green mixture composition on combustion temperature, particle morphology, and chemical composition of the aluminum nitride obtained has been studied. The synthesis optimum conditions have been determined.

During our investigations we observed that an increase in the synthesis temperature resulted in enlargement of AlN grains; at T=2350°C the grains were maximum in their size (about 20-30  $\mu\text{m}$ ) and edged in their form. Besides, the product partials sintering took place. When the aluminum content in the green mixture was 70 %, the combustion temperature exceeded the dissociation temperature of aluminum nitride. Under such terms AlN particles of various shape and size were formed. When the synthesis was carried out at the green mixture combustion limit, the product of synthesis consists of separate particles of submicron size. The specific surface of the AlN obtained ranged from 0.1 to 2.5  $\text{m}^2/\text{g}$  depending on a synthesis temperature mode. The green mixture composition and, therefore, the synthesis temperature significantly affected the purity of the synthesized aluminum nitride. When the synthesis temperature was close to the dissociation temperature of AlN, we obtained the purest product.

This work is supported by Russian Foundation for Basic Research, grant RFBR 00-15-99054.

**P-1-207: The Role of Aluminum in Phase Formation of Products at Combustion of Ternary System Mo-Si-Al**

*U. Rezabal<sup>1</sup>, I. Agote<sup>1</sup>, M. Guitérrez<sup>1</sup>, A. Sargsyan<sup>2</sup>, S. Kharatyan<sup>2</sup>*

<sup>1</sup>*INASMET Foundation (Spain)*

<sup>2</sup>*Institute of Chemical Physics NAS of Armenia (Armenia)*

The aim of this work is to study the combustion of ternary system Mo-Si-Al and the role of aluminum in the phase and microstructure formation of products. For this purpose molybdenum wires were used which were imbedded into a powdered Mo-Si-Al mixture and the behavior of large particles of metal both in combustion front and post combustion zone was simulated. It was shown that, depending on combustion temperature (reaching by changing the ratio of reagents) and thermal conductivity of the sample medium surroundings, it was possible to elongate the different combustion stages and study the phase formation process. It was found out that the interaction of the reagents in the system studied began at a lower temperature than in the case of binary system Mo-Si caused by the presence of liquid phase at a lower temperature. It was also observed that the aluminum activated the process of dilution of molybdenum particles in the liquid phase (silicon-aluminum eutectic) and intensified the process of phase and structure formation. Two main complex silicide phases were obtained during this study: one aluminum-rich and the other silicon-rich. The final product synthesized is single-phase  $\text{Mo}(\text{Si}_{0.8},\text{Al}_{0.2})_2$  which has a better technical application than  $\text{MoSi}_2$ .

**P-1-106: Self-Propagating High-Temperature Synthesis of Chromium-Substituted HTSC**

**$\text{RBa}_2\text{Cu}_{3-x}\text{Cr}_x\text{O}_{7-y}$  (R = Y; La; Nd; Sm; Yb)**

*M.V. Kuznetsov<sup>1</sup>, Yu.G. Morozov<sup>1</sup>, I.P. Parkin<sup>2</sup>, Q.A. Pankhurst<sup>3</sup>*

<sup>1</sup>*Institute of Structural Macrokinetics and Materials Science RAS*

*Chernogolovka, Moscow Region, 142432 Russia*

<sup>2</sup>*Department of Chemistry, University College London, 20 Gordon Street, London, WC1H 0AJ, UK*

<sup>3</sup>*Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK*

As systematic study of the structural, magnetic and superconducting properties of SHS-prepared HTSC  $\text{RBa}_2\text{Cu}_{3-x}\text{Cr}_x\text{O}_{7-y}$  (R = Y; La; Nd; Sm; Yb) compounds doped by trivalent  $\text{Cr}^{3+}$  has been performed for  $x = 0 \div 0.25$ . SHS reactions were performed in the green mixtures of appropriate rare-earth (III) oxides, copper as a source of fuel, barium peroxide and alkaline perchlorates as a solid oxidizers – inner sources of oxygen in the combustion reaction.

X-ray powder diffraction, magnetic susceptibility, pycnometric density, oxygen content measurements etc. has been made. The ionic radii and orbital structure of 3-d elements a close to those of Cu, and we expected that Cr will occupy the Cu sites of 123 structure. Most substitutions does not significantly modified the  $\text{RBa}_2\text{Cu}_3\text{O}_{7-y}$  cell parameters. Orthorhombic  $a$ ,  $b$  and  $c$  parameters were found to slightly increase in all the cases with  $x$  while  $a/b$  and  $c/b$  parameters were constant and independent from  $x$  for all the R, but increased with ionic radii of R (from 0.982 and 2.994 for Y to 1.018 and 3.079 for Yb).

The magnetic character of the doping element appears to decrease  $T_C$  with  $x$ . This indicates that disorder plays an important role in the superconductivity. Maximum level of substitution provides a sizable change in  $T_C$ , but is not large enough to destroy superconductivity completely. The experimentally observed  $T_C$  suppression can be related to the “classical” theory of Abrikosov-Gorkov and be dependent from the localized magnetic moment of magnetic Cr-impurities.  $T_C$  reducing were accompanied by magnetic susceptibility increase with  $x$ . The oxygen content of the samples increased with  $x$  as directly after SHS as after post-SHS treatment of the products in an oxygen flow. However in all the cases the oxygen content was not high than 7.0, even for highest degree of substitution. UV absorption (%) were found to be reduced with  $x = 0 \div 0.25$  for Y from 1.77 to 1.22 % and for Nd from 1.86 to 1.18 %. Chromium doping led also to increasing of

thermostability and ortho-tetra transition temperature in all the systems in the temperature range 20-1000 °C.

This work is supported by Russian and Belorussian Foundations of Basic Researches, grant RFBR 00-03-81193 Bel2000\_a, Russian Foundation for Basic Research, grants RFBR 00-15-99054, 00-03-40141i and INTAS YSF-00-22.

### **P-2-121: Self-Propagating High-Temperature Synthesis of $Ti_3SiC_2$**

*Y. Khoptiar, I. Gotman, E.Y. Gutmanas*

*Faculty of Materials Engineering, Technion, Haifa 32000, Israel*

The compound  $Ti_3SiC_2$  belongs to a unique group of ternary ceramics known for their excellent high-temperature mechanical properties, high oxidation resistance, good machinability and high electrical and thermal conductivities. In this work  $Ti_3SiC_2$  was produced from elementary powder blends via Thermal Explosion (TE) mode of Self-propagating High-temperature Synthesis. The Thermal Explosion has an advantage of the lower furnace temperatures and considerably shorter processing times compared to the related Reactive Hot Pressing method (RHP).

The kinetics of the TE processing was studied by close monitoring of the temperature evolution in the samples during the synthesis. It was found that  $TiC$  and  $Ti_5Si_3$  were formed at the first stage of the synthesis. Under certain thermo-physical conditions almost full conversion of reagents into products took place, and  $Ti_3SiC_2$  was formed. In addition, measurable amounts of  $TiC$  and silicides could be detected in the thermally exploded samples. As a result of the rapid processing, a relatively fine (less than 10  $\mu m$ ) microstructure was obtained. The application of moderate uniaxial pressure during TE synthesis (Reactive Forging) allowed us to produce near fully dense samples. The effect of the initial blend composition and powder size on the phase composition, microstructure and porosity of the product was studied.

The obtained results will be incorporated into a general model of pressure-assisted synthesis that allows to predict the occurrence of SHS in various reactive systems.

### **P-1-201: SHS as Source of Heat**

*V.D. Zhigarev, V.A. Ovchinnikov*

*State Scientific Center RF – Central Research Institute of Chemistry and Mechanics*

*Nagatinskaya str., 16a, Moscow M-487, 115487, Russia, fax: (095) 116-78-18*

Developed in CNIIHM heat-generating reactor (HGR) can be an aid in solving the basic problems determining the development of SHS-technology: making a production with a continuous technological cycle; utilizing heat energy; regulating the process of synthesis products structurilization.

The procedure of heat calculation presented, which was confirmed by the experimental data, demonstrated that the time of synthesis products cooling in HGR is by 2-3 orders of magnitude shorter as compared with conventional SHS-reactors. This motivates the possibility of using HGR as regenerative heat exchanger providing: several times increase in cyclic recurrence of reactor operation; intensive heat transfer to gaseous heat-transport agent; regulation of the rate of synthesis products cooling – on the one hand, at the expense of time lag changing before a coolant start, on the other hand, at the expense of temperature and burning rate decrease because of coolant opposing flow (up to putting out of SHS-process).

### **P-2-109: SHS-Assisted Preparation of Ceramic Composites**

*L. Stobierski, A. Gubernat*

*Department of Advanced Ceramics*

*Faculty of Materials Engineering and Ceramics*

*Academy of Mining and Metallurgy, Cracow, Poland*

Rational shaping of ceramic materials' microstructure with regard to both phase composition and geometry of mutual phase distribution constitutes the basis for shaping physical and chemical

properties of materials. Significant difficulties exist in classical ceramic practice of powder mixtures sintering resulting from necessity of obtaining multiple compounds in the form of chemically pure powders having desirable grain size distribution. Combination of sintering process of the powder constituting the composite matrix with simultaneous synthesis of the dispersed phase compound can be one of the methods allowing elimination of these difficulties. Research on combination of hot-pressing technique with Self-propagating High-temperature Synthesis has been conducted in the pseudo-binary  $\text{SiC}-\text{TiB}_2$  system.

Titanium diboride was the phase synthesised during sintering of  $\text{SiC}$  powder. Substrates for  $\text{TiB}_2$  synthesis were titanium hydride and boron. Composite materials with  $\text{TiB}_2$  content in the range of 0 – 30 vol. % have been obtained using this technique. These materials were tested in order to define the changes in physical composition of the materials caused by increasing content of the dispersed phase. Changes in the coefficient of thermal expansion, bending strength, hardness and elastic properties were determined.

#### **P-2-58: SHS Densification of Compounds Resistant to High-Temperature Action**

*A.N. Pityulin, I.P. Borovinskaya*

*Institute of Structural Macrokinetics and Materials Science, RAS*

*Chernogolovka, Moscow Region, 142432, Russia*

Nowadays pseudoalloys of tungsten-copper, special graphite with the operation surface covered by tungsten and other compounds are used as materials operating under the terms of high-temperature and erosion action. These materials have some disadvantages, such as high density, low utilization factor or a complicated production technology.

The aim of our work was to obtain the compounds which could resist gaseous flows containing abrasive inclusions and characterized by  $T>3000^\circ\text{C}$ ,  $P>1.5$  MPa by the method of SHS densification.

As the result we produced cylindrical samples of 70-100 mm in diameter, 25-70 mm in height with a hole in the center ( $d=10-20$  mm) from the alloys of  $\text{ZrB}_2-\text{SiC}-\text{C}$  and  $\text{TiB}_2-\text{Cu}$  with copper content being from 10 to 50 %. Optimization of technological modes of the method of SHS densification allowed us to obtain the alloys of high homogeneity and a porosity of less than 1.5 %.

The obtained items were tested under the following terms:

flow temperature -  $2800^\circ\text{C}$ , pressure - 1.6 MPa, solid phase content - 20 %, testing time - 20 s, medium - oxidizing. During our investigations the both materials showed high thermal strength and minimum erosion.

Any further increase in gaseous flow temperature and pressure indicated that the alloy of  $\text{TiB}_2-\text{Cu}$  was better than the alloy of  $\text{ZrB}_2-\text{SiC}-\text{C}$ . At  $T_{\text{test}}=4400^\circ\text{C}$ ,  $P=1.75$  MPa, and testing time of 7-9 s thermal strength and erosion stability of the alloy of  $\text{TiB}_2-\text{Cu}$  were considered to be satisfactory.

Thus, our investigations have proved that the method of SHS densification is an efficient method of obtaining materials resistant to high temperature and erosion action.

This work is supported by Russian Foundation for Basic Research, grant RFBR 00-15-99054.

#### **P-2-15: SHS of Composite Powders of Refractory Compounds and Compact Materials on Their Base**

*S.S. Mamyan, D.Yu. Belov, I.P. Borovinskaya, A.N. Pityulin, S.S. Ordanyan*

*Institute of Structural Macrokinetics and Materials Science*

*Chernogolovka, Moscow 142432 Russia*

The paper investigates complex SHS composite materials. It is shown that fine composite powders are possible to be obtained in the systems of  $\text{TiC}-\text{SiC}$ ,  $\text{TiB}_2-\text{B}_4\text{C}$ ,  $\text{TiB}_2-\text{B}_4\text{C}-\text{TiC}$ ,  $\text{TiB}_2-\text{SiC}$ , etc.

Optimum conditions (a ratio of initial components, medium pressure, etc.) for synthesizing the above mentioned powder materials are determined by the method of thermodynamic analysis. In the case of partial substitution of initial elemental powders by their oxides (Ti with  $\text{TiO}_2$ , B with  $\text{B}_2\text{O}_3$ , etc.), the exothermic nature of initial components interaction is shown to favor the oxides

reduction with the following gaseous products liberation (TiO, CO, Co<sub>2</sub>, B<sub>2</sub>O<sub>3</sub>, B<sub>2</sub>O<sub>2</sub>, B<sub>2</sub>O, etc.), which provides the combustion product size reduction. The investigation results of densification of these composite materials by the STIM technological method are presented in the paper. It is underlined that if the material is obtained from elements without oxide addition, its grain size is significantly larger. The structure and properties of two types of compact material are compared: those obtained by the STIM technology and by the method of isothermal sintering.

After analyzing the investigation results, it is possible to find better application for these materials in various fields of engineering.

This work is supported by Russian Foundation for Basic Research, grant 00-15-99054.

#### **P-2-17: SHS of Lead Hexaferrite**

*K. S. Martirossyan<sup>1</sup>, P. B. Avakyan<sup>1,2</sup>, M. D. Nersesyan<sup>2</sup>*

*<sup>1</sup>Scientific and Industrial Center SHS, Yerevan, Armenia*

*<sup>2</sup>Institute of Structural Macrokinetics and Materials Science, Chernogolovka, Russia*

Traditional ceramic synthesis methods do not produce a high quality stoichiometric product of PbFe<sub>12</sub>O<sub>19</sub> due to the high volatility of toxic lead oxide, PbO. This inability to produce pure PbFe<sub>12</sub>O<sub>19</sub> limits its application despite its high functional properties. The high conversion rate (i.e., short synthesis time) during SHS helped to overcome these difficulties. SHS was used to produce lead hexaferrite, PbFe<sub>12</sub>O<sub>19</sub>, via combustion of either PbO-Fe-Fe<sub>2</sub>O<sub>3</sub> or PbO<sub>2</sub>-Fe-Fe<sub>2</sub>O<sub>3</sub> mixtures in oxygen. The variation of Fe content in the solid mixtures was used to control the synthesis conditions and the product composition. The product weight control and its analysis showed that complete conversion of the reactants occurred at Fe content of 15% (combustion temperature about 1590K), while 4% mass loss due to evaporation of PbO during combustion occurred only for mixtures containing more than 20% Fe (temperatures exceed 1620K). The evolution of the chemical and phase composition and microstructure of the combustion product was investigated using layer-by-layer analysis of the quenched samples. Analysis indicated that the stoichiometric composition of lead hexaferrite formed 3-4 seconds after the combustion front passed through the sample. The naturally cooled product had a hexagonal structure with lattice constants of  $a=5.87$  Å,  $c=23.11$  Å and  $c/a=3.936$ . In some cases, depending on the combustion temperatures and cooling rates, product also included monocrystals of lead hexaferrite from 0.2 to 1.2 mm in diameters.

Electromagnetic parameters of the synthesized ferrite were:  $\sigma_s = 38$  T m<sup>3</sup>10<sup>-7</sup>/kg,  $\sigma = 15$  T m<sup>3</sup>10<sup>-7</sup>/kg,  $H_c = 47$  kA/m and  $\rho = 3.6 \cdot 10^7$  kOm m. Magnetic properties of SHS produced lead hexaferrite based isotropic permanent magnets (containing SiO<sub>2</sub> as additive) were characterized as:  $B_r$  – (0.15–0.24) T,  $H_{cB}$  – (100–130) kA/m,  $H_{cM}$  – (130–187) kA/m, magnetic energy  $(BH)_m$  – (3.8 – 9.6) kJ/m<sup>3</sup>. Thus, SHS may serve as an alternative technology for the manufacture of hard ferrite materials for industrial applications.

#### **P-2-149: SHS of La-Ca-Cr Complex Oxides for High-Temperature Applications**

*Sy-Chyi Lin<sup>1</sup>, I. J. Lee<sup>2</sup>, M. D. Nersesyan<sup>2,3</sup>, V. I. Yukhvid<sup>3</sup>, R. Wilkins<sup>1</sup>, Dan Luss<sup>2</sup>*

*<sup>1</sup>NASA Center for Applied Radiation Research, Prairie View A&M University Prairie View, TX 77446*

*<sup>2</sup>Chemical Engineering Department, University of Houston, Houston, TX 77204*

*<sup>3</sup>Institute of Structural Macrokinetics and Materials Science, RAS, Chernogolovka, Russia, 142432*

Lanthanum chromite, LaCrO<sub>3</sub>, has been used in solid oxide fuel cells and high temperature furnaces because of its thermal and chemical stability and unique electrical properties at high temperatures. However, a rather low density is usually obtained when LaCrO<sub>3</sub> is sintered in air. A reduced oxygen partial pressure is required for good sintering that complicates the process. Other way to increase the LaCrO<sub>3</sub> density during sintering in air is doping of lanthanum chromite by metals of IIA group. We used self-propagating high-temperature synthesis to produce Ca-doped LaCrO<sub>3</sub> powders, suitable for sintering in air. La<sub>0.9</sub>Ca<sub>0.1</sub>CrO<sub>3</sub>, La<sub>0.9</sub>Ca<sub>0.1</sub>Cr<sub>0.95</sub>O<sub>3</sub>, and

$\text{La}_{0.9}\text{Ca}_{0.1}\text{Cr}_{0.9}\text{Ca}_{0.1}\text{O}_3$  were synthesized using different reactions. Combustion conditions were used to study the impacts of SHS variables on the product quality. Optimal sintering conditions in air, generating high quality products were developed. Electrical conductivity of sintered articles was measured at different temperatures.

The work is supported by the CRDF Grant #RC2-2213.

#### **P-2-148: SHS of Li-Based Complex Oxides for Battery Application**

*Sy-Chyi Lin<sup>1</sup>, M. D. Nersesyan<sup>2,3</sup>, R. Wilkins<sup>1</sup>, Dan Luss<sup>2</sup>*

<sup>1</sup>*NASA Center for Applied Radiation Research, Prairie View A&M University Prairie View, TX 77446*

<sup>2</sup>*Chemical Engineering Department, University of Houston, Houston, TX 77204*

<sup>3</sup>*Institute of Structural Macrokinetics and Materials Science, RAS, Chernogolovka, 142432, Russia.*

The development of a light-weight compact-size power sources with prolonged cycle life is crucial to the future mobile communication such as cellular phones, portable personal computers and many other entertainment and military applications. Lithium batteries are among the most extensively studied power sources because of its high capacity, stable electricity current, and long life cycle. However, the synthesis of the battery materials is time and energy consuming. We used SHS to produce  $\text{LiMeO}_2$  (Me: Mn, Ni and Co),  $\text{LiMn}_{0.5}\text{Co}_{0.5}\text{O}_2$ ,  $\text{LiMn}_2\text{O}_4$  and  $\text{Li}_2\text{MnO}_3$  complex oxides having potential for battery applications. The relationship between the synthesis conditions and product properties was investigated. Product phase and chemical compositions were analyzed by XRD and EMPA. Powders were tested for their rate capacity, capacity, cycle life, and electrochemical impedance spectroscopy.

#### **P-2-56: SHS of Magnesioferrites**

*P.B. Avakyan, V.G. Andreev, G.D. Grigoryan, H.V. Aboyan, A.M. Petrosyan, N.M. Martirosyan*

*Scientific and Industrial Centre SHS, Yerevan, 375010 Armenia*

Soft magnetic Mg-Zn ferrites find widespread application in modern engineering, supplanting Ni-Zn ferrites due to availability and low prices of Mg-containing raw materials, smaller weight and increased level of frequent properties. In this study, the SHS of Mg-Zn ferrite powders, the kinetics of their sintering and the properties of final products were investigated. Synthesis has been carried out in the  $\text{MgO-ZnO-Fe}_2\text{O}_3-\text{Fe-O}_2$  system using functional additives. The impact of synthesis conditions on the chemical and phase compositions of SHS-powders and their properties was investigated.

The sintering kinetics of ring wares, made by pressing of SHS-powders granulated with a binder, was investigated at temperatures up to  $1450^\circ\text{C}$ . The gas-penetrability of wares grew at the early stages of sintering and sharply decreased at the intermediate stages. The shrinkage factor grew monotonously and reached its practically constant value of 1.08 at temperature  $1250^\circ\text{C}$ . The maximum level of properties was reached for wares with density exceeding  $4.75 \text{ g/cm}^3$  and zero gas-penetrability. For  $\text{Mg}_{0.54}\text{Zn}_{0.46}\text{Fe}_2\text{O}_4$  based ferrites doped with 2 wt.%  $\text{MnO}$ , an initial magnetic permeability ( $\mu$ ) within the range from 580 to 630 was obtained at the relative tangent of core losses ( $\text{tg}\delta/\mu$ ) less than  $15 \cdot 10^{-6}$  (at 100 kHz and field amplitude of 0.8 A/m).

Supported by the US Civilian Research and Development Foundation (CRDF) Grant AC2-2211.

#### **P-2-71: SHS-Processing of Molybdenum Containing Sulphide Raw Materials**

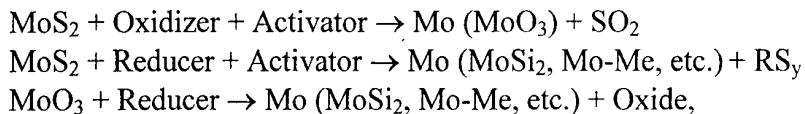
*A.R. Sargsyan, S.L. Kharatyan, A.G. Dorunts*

*Nalbandyan Institute of Chemical Physics NAS of Armenia, 375044, Yerevan, Republic of Armenia*

The modern metallurgy has a wide selection of ways for processing sulfur-containing raw materials with the aim of extracting metals. However, the large majority of pyrometallurgical processes,

especially those conducted at high temperatures and pressures are multistage, power-consuming and usually break the allowable ecological norms because of imperfectness of the equipment or technological scheme used.

In the work thermodynamic analysis of oxidation-restoration conditions for sulfides and oxygen-containing materials were carried out using various kinds of initial raw materials. Adiabatic combustion temperatures and equilibrium compositions of products were calculated. An opportunity of SHS process realization is estimated and optimum conditions for producing molybdenum and materials on its basis from the thermodynamic point of view were determined. Alongside with it experimental check of the opportunity of SHS method application at various stages of processing of sulfides and oxygen-containing compounds of molybdenum are performed. Some important laws of layer by layer combustion of initial mixture are revealed. Interactions proceeding are listed below:



where  $\text{RS}_y$  is the sulfur-containing gaseous or solid substance, easily separated from a target product.

Reasoning from experimental studies of these reactions it was shown the opportunity for application not only simple, but various combined oxidants and restorers as well. Combustion temperature and velocity for various mixtures were estimated, phase and chemical composition of final products were determined. It was shown that the character of proceeding of these as well as the composition of final products can be changed in a wide range of values, and products obtained can be both as melts and powders. The addition of various fluxing materials to the melt allows one to separate practically completely the metal part of melt from formed slag.

It was shown by electron-microscopic studies of molybdenum-rich metal ingots that the microstructure and homogeneity of the material strongly depend on conditions of process performing.

### **P-1-157: SHS Wave Propagation in Mg-Si System**

*D. Horvitz, I. Gotman*

*Department of Materials Engineering, Technion, Haifa 32000, Israel*

Magnesium silicide,  $\text{Mg}_2\text{Si}$  is an intermetallic compound having several desirable properties for structural applications, such as very low density ( $2 \text{ g/cm}^3$ ), and relatively high hardness (550 HV). In addition, the extraordinary thermo-physical properties of  $\text{Mg}_2\text{Si}$  make it a potentially attractive material for thermo-electric power generators and heat storage capacitors.

The production of  $\text{Mg}_2\text{Si}$  a major engineering problem as no conventional casting is possible due to the very high Mg vapor pressure at the silicide melting temperature. On a laboratory scale,  $\text{Mg}_2\text{Si}$  is fabricated by hot pressing of the powder produced by mechanical alloying of the elemental Mg and Si - a process that introduces a large amount of impurities into the product.

In the present research, the possibility of SHS synthesis of  $\text{Mg}_2\text{Si}$  from a fine Mg-Si powder blend has been investigated. The synthesis reaction,  $2 \text{ Mg} + \text{Si} \rightarrow \text{Mg}_2\text{Si}$ , is only weakly exothermic, with the calculated adiabatic temperature  $T_{ad} = 1100 \text{ K}$ . Despite the low  $T_{ad}$  value, a stable combustion wave propagation was observed at room temperature. Temperature profiles in several points along the wave propagation direction were measured with high degree of accuracy. The material obtained was characterized employing x-ray diffraction and SEM/EDS. In the course of SHS synthesis, full conversion of the Mg and Si reagents into the  $\text{Mg}_2\text{Si}$  compound was obtained, with very small amount of  $\text{MgO}$  detected in the final product. It is assumed that Mg vapor phase plays an important role in mass transfer during SHS wave propagation in Mg-Si system.

**P-1-99: Structural Processes Formation of Functional Porous Materials in Combustion of Metallothermic Systems**

*A.I. Kirdyashkin, R.A. Yusupov, Yu.M. Maksimov, V.D. Kitler*

*Department of Structural Macrokinetics of the Tomsk Scientific Center of Siberian Branch of Russian Academy of Sciences, Tomsk, 634021 Russia*

Complex investigations of the structure and the composition of porous composite SHS materials of corundum-metal-like alloys type were conducted. Mechanisms of influence of conditions of SHS reaction proceeding on formation conditions of macro-and microstructure of the product were defined. Possibilities of purposely directed porous material parameter regulation were shown. Test data of articles from porous ceramic material on mechanical strength, corrosion and thermal resistance, gas-hydrodynamic permeability show that articles parameters exceeded analogues, obtained according conventional ceramic methods. Possibilities of use of articles as filters for purification of liquids and gases under effect of chemically aggressive and high temperature media are proved.

**P-2-46: Structure and Properties of Diamond-Containing TRESS-Coatings Produced Using New One High Frequency Installation "Alier-Metal"**

*E.I. Kharlamov<sup>1</sup>, A.E. Kudryashov<sup>1</sup>, E.A. Levashov<sup>1</sup>, M. Ohyanagi<sup>2</sup>, S. Hosomi<sup>3</sup>, M. Koizumi<sup>2</sup>*

*<sup>1</sup>SHS-Center of Moscow Steel and Alloys Institute (Technological University) and the Institute of Structural Macrokinetics and Material Science of RAS*

*Leninsky prospect, 4, 164 Moscow 119991, Russia*

*<sup>2</sup>Ryukoku University, Yokotani 1-5, Seta, Ohtsu City 520-21, Japan*

*<sup>3</sup>Tomei Diamond Co., Ltd, Joto 4-5-1 Oyama-city, 323, Japan*

The present work has studied the process of structure formation and the properties of diamond-containing coatings produced by thermoreactive electrospark surface strengthening (TRESS) using a new one promising high-frequency installation "Alier-Metal".

As compared with the analogues of "Elitron" series, the installation makes it possible to vary the impulse discharge frequency in a wide range: from 20 Hz through 3,000 Hz in 11 power modes. This permits to obtain coatings of various composition, thickness, and surface quality. The new installation makes use of the last developments and the electrical circuits to noticeably raise the installation performance factor and reduce its dimensions and weight several times.

Series of investigations were carried out in the "Alier-Metal" installation with the use of mixture electrodes on the base of Ti+Al+diamond and Ti+B+diamond at different impulse discharge energies. A comparative X-ray phase analysis show that diamond-containing coatings produced in the new installation contain borides and intermetallic compounds the amounts of which are several times as large in comparison with the analogous coatings produced using "Elitron-22A" in the same systems. The content of diamond in the coating produced in the new installation achieves to 40 %. High-frequency modes used in the installation gives rise to more profound chemical transformation among the charge components in the coating and on the surface resulting in improving the mechanical properties of the coating, in increasing the coating wear resistance in particular.

**P-2-111: Structure Changes Resulting from Annealing of AlN-SiC System Synthesised Using SHS Method**

*Z. Wegrzyn, L. Stobierski, M. Bucko*

*Department of Advanced Ceramics, Faculty of Materials Engineering and Ceramics Academy of Mining and Metallurgy, Cracow, Poland*

Both AlN and SiC can crystallise in the wurtzite structure (2H). In this structure the difference in  $a$  and  $c$  lattice parameters between AlN and SiC are lower than 1.4 %, which makes creation of solid solution possible. The syntheses of the AlN-SiC composites in 50/50 mole % ratio have been realised using a combustion method of Self-propagating High-temperature Synthesis. The mixtures

of aluminium, silicon and carbon powders have been used as reactants. Initiation of the SHS has been realised at 150°C in nitrogen atmosphere. Additives B, C,  $Y_2O_3$ ,  $Al_2O_3$ , have been used as sintering aids in the following patterns: B + C,  $Y_2O_3$  +  $Al_2O_3$  and B + C +  $Y_2O_3$  +  $Al_2O_3$ . One sample has additionally been sintered without any additives. Samples have been densified by hot pressing under the pressure of 25 MPa at 2050°C. Annealing has been undertaken over a temperature range between 1600 and 1800°C in nitrogen atmosphere for periods of up to 50 hours. The sintered and annealed AlN-SiC solid solutions have been analysed structurally by X-ray diffraction (XRD) and transmission electron microscopy (TEM). Structure changes have been observed in the annealed samples.

#### **P-2-100: Surface Combustion of Chromium in Nitrogen**

*B.Sh. Braverman, M.Kh. Ziatdinov Yu.M. Maksimov*

*Department of Structural Macrokinetics of the Tomsk Scientific Center of  
Siberian Branch of Russian Academy of Sciences, Tomsk, 634021 Russia*

Combustion of metal powders in gaseous oxidizer can be carried out in one of two different modes: layer-by-layer or surface. Transition from one mode to another is defined by the parameters of filtration flow of oxidizer to the reaction zone. From these two modes surface mode is less studied. This paper presents some results of investigation of surface combustion in chrome-nitrogen system. By means off changing scheme of combustion it become possible to observe a distortion of combustion front caused by the surface mode. Temperature was measured in some points of distorted front. The scheme, used in work, allows to study the evolution of surface combustion front's form and regularities of transition from layer-by-layer mode to surface one. Visualization of surface combustion front can help to explain some particularities of product's forming in chromium- nitrogen system.

#### **P-1-86: Synthesis of Chemically Non-Uniform Materials from a Homogeneous Green Mixture in the Thermal Explosion Mode**

*B.S. Seplyarskii, T.P. Ivleva, A.G. Merzhanov*

*Institute of Structural Macrokinetics and Materials Science*

*Russian Academy of Sciences, Chernogolovka, 142 432 Russia*

For the recent years thermal explosion has been found to be an efficient synthetic approach to production of inorganic materials. IN this case, analysis of the occurring phenomena cannot be reduced to determination of only critical conditions and calculation of the induction period of ignition like it was done in the classical studies by N.N. Semenov and D.A. Frank-Kamenetsky. On the contrary, from the practical viewpoint, the greatest attention should be focused at the chemical composition of the final products, which above all determines the physicochemical properties of the resultant materials. Therefore all stages of the initial substance conversion to the product should be followed by the theoretical analysis of thermal explosion. The possibility of synthesis of non-uniform materials from a homogeneous green mixture in the thermal explosion mode is for the first time reported in the present paper on the example of the initial substance conversion in accord with the scheme of competing reactions.

The following model process is considered. A flat layer of a condensed substance of a 2L thickness capable of exothermic converting is open to the contact with the environment. The substance and the medium have the same temperature  $T_0$ . The substance ignition and combustion is initiated by its self-heating. It is supposed that chemical conversion of the initial component A can proceed via two routes  $A \rightarrow B$  and  $A \rightarrow C$  (competing reactions). Each route is characterized by its own set of the kinetic parameters  $k_{0,i}$ ,  $E_i$  and thermal effect  $Q_i$ . It also assumed that the substance-environment heat exchange obeys the Newtonian law and is characterized by the coefficient of heat exchange  $a$ , the initial substance and the reaction products are condensed matters.

Analysis of the initial set of equations performed by the approximate analytical and numerical methods has allowed determination of the necessary and sufficient conditions of production of both

non-uniform (gradient) and homogeneous materials in the regime of thermal explosion. It has been shown that synthesis of inhomogeneous material is possible only at high values of the Biot criterion, when at the stage of propagation, chemical conversion is localized in the vicinity of the maximum temperature, and at an alternating ratio of the reaction rate of one of the routes to that of the other under the adiabatic conditions of thermal explosion occurrence.

It has been found that dilution of the initial substance with inert additives is a universal method of improving the final product homogeneity. The conditions when the final product composition depends not only on the kinetic and thermophysical characteristics of the initial substance but also on the Biot criterion value have been determined.

#### **P-2-192: Synthesis of Dense *in-situ* $\text{Al}_2\text{O}_3/\text{TiB}_2$ Composites via Thermal Explosion under Pressure**

*Y. Gutmanas, I. Gotman, M. Shapiro*

*Faculty of Materials Engineering, Technion, Haifa 32000, Israel*

SHS with highly exothermic reaction can provide the possibility of processing dense *in-situ* ceramic composites with high concentration of hard particles that do not participate in the reaction. Such composites can be used as wear resistant tool materials.

In the present research, *in-situ*  $\text{Al}_2\text{O}_3/\text{TiB}_2$  composites were produced from fine  $\text{B}_2\text{O}_3$ -Al-Ti and  $\text{B}_2\text{O}_3$ -Al-TiO<sub>2</sub> powder blends with addition of fine  $\text{TiB}_2$  particles, acting as a diluent, employing Reactive Forging, RF (thermal explosion mode of SHS under pressure) and Reactive Hot Pressing method (RHP) processing routes. The RF process has an advantage of lower furnace temperatures and considerably shorter processing times compared to the related RHP method.

The kinetics of the RF processing was studied by close monitoring of the temperature evolution in the samples during the synthesis. As a result of the rapid processing, a very fine microstructure was obtained. The application of moderate uni-axial pressure during Reactive Forging allowed production of near fully dense samples. The effect of blend composition with various volume fractions of diluent on microstructure, density and mechanical properties of the product was studied. Microstructure was characterized by X-Ray diffraction and SEM/EDS methods. Thermal properties of the material during the synthesis were also investigated. The results obtained were used for preparation of  $\text{Al}_2\text{O}_3/\text{TiB}_2$  based composites with cubic BN as a diluent.

#### **P-1-69: Synthesis of Materials Based on Niobium Carbides, Borides, and Nitrides and Study of Their Catalytic Properties**

*E.H. Grigoryan<sup>1</sup>, A.S. Rogachev<sup>1</sup>, H.E. Grigoryan<sup>1</sup>, A. Gavrilidis<sup>2</sup>, V.N. Borsh<sup>1</sup>*

*<sup>1</sup>Institute of Structural Macrokinetics and Materials Science RAS, Russia*

*<sup>2</sup>University College London, UK*

Materials based on nitrides, carbides and borides of niobium with use of nitrides and other compounds as initial reagents were synthesized. The catalytic activity of obtained materials in methane oxidation, CO oxidation, and ethylene hydrogenation was studied.

The catalytic system of NbN on alumina and NbB<sub>2</sub> on alumina were shown to exhibit catalytic activity for CO oxidation at the temperature of 250-300°C; and NbN on alumina is also active in hydrogenation of ethylene at the room temperature. The stability of the synthesized catalytic systems was investigated by performing many-cycle experiments without change the catalysts. The catalysts were found to retain their activity for a long time, and the activity of the NbN – based catalyst even increased after the first experiments.

#### **P-2-22: Synthesis, Structure and Properties of Conducting $\text{TiB}_2$ -AlN-Based Ceramics**

*V.A. Bunin, A.V. Karpov, M.Yu. Senkovenko*

*Institute of Structural Macrokinetics and Materials Science RAS,*

*Chernogolovka, 142432 Russia*

In this work, synthesis of conducting  $\text{TiB}_2$ -AlN-based system with solid green reagents has been investigated in filtration combustion mode at elevated nitrogen pressure (from 20 to 300 MPa).

Effect of pressure on combustion rate and content of free aluminum in end products was studied. The green mixture composition dependence of combustion rate was determined. Composition of the end product, as well as porosity, volume resistivity and bending strength of synthesized products were examined by XRD and chemical analysis. Structural peculiarities of the SHS-synthesized system and critical concentration of titanium diboride (19 vol.%) in the composition, resulted in discontinuous change in material properties, allow to suggest that the change of conducting properties can be explained by generated fractal structures.

This work is supported by Russian Foundation for Basic Research, grants RFBR 00-03-32481a, 00-15-99054.

#### **P-2-98: TiC Synthesis in a Titanium Container: Experiments and Modeling**

*M.-F. Beaufort<sup>1,3</sup>, S. Dubois<sup>1,3</sup>, N. Karnatak<sup>1</sup>, A. Aoufi<sup>2,3</sup>, D. Vrel<sup>2,3</sup>.*

*<sup>1</sup>CNRS – LMP, Bât. SP2MI, BP 30179, Boulevard P. et M. Curie  
86960 Futuroscope Cedex, France*

*<sup>2</sup>CNRS – LIMHP, 99 avenue J.-B. Clément, 93430 Villeurbanne, France*

*<sup>3</sup>CNRS – GFA, GDR 2391, J.-C. Nipce, LRRS, 9 av. A. Savary, B.P. 47870  
21078 Dijon Cedex, France*

The numerous advantages of SHS have very often been pointed out. However, the materials produced are systematically very porous. Except in some cases where this porosity can be used (e.g. in catalysts), this characteristic is a serious drawback. Indeed, a great amount of energy will be required to achieve a large relative density which is necessary for most applications. Such is the case for thermo-mechanical applications, where the highest density achievable is required. Beside the energetic point of view, if the densification could be made with no additional energy, using only the heat provided by the reaction, smaller grain sizes could be obtained, and therefore better mechanical properties as it is well known in the so called nanostructured materials.

As natural sintering does not occur during the post combustion stage of TiC synthesis, we are presently investigating a high isostatic pressure densification of a sample just after its synthesis. However, in order to have a better understanding of the different phenomena occurring during the combustion synthesis, we decided to start our investigation by focusing on the initiation and propagation conditions of the reaction performed in an open container.

Ti and C particles, 40 and 7  $\mu\text{m}$  diameters respectively, are thoroughly mixed in a turbula in order to obtain a random mixture of the reactants. Such a mixture is thus inserted in a Ti container (3 cm length and 1 cm diameter). An uniaxial pressure of 1600 bars is thus applied to the loose array of Ti and C particles; the resulting compact density, before the combustion reaction, is about 50 %. Self propagating high temperature synthesis of TiC is thus initiated, at room temperature and atmospheric pressure, using a graphite resistor.

Two thicknesses of the Ti container have been used (0.2 and 0.7 mm). X-Ray diffraction analysis allows one to determine the completeness character of the combustion synthesis (i.e. initiation and propagation). In a next step, we have focused on the interface between the Ti container and the TiC reacted zone using scanning electron microscope (SEM) and microanalysis. Experimental results demonstrate that, for the thinner Ti container, the melting point of the Ti container is reached whereas it does not melt during the combustion reaction for the thicker one. The modeling part of our study is based on reaction-diffusion enthalpy balance which takes into account the various phase transitions and the exothermic TiC synthesis reaction. Special care was given to the interface between sample and container in the form of specific boundary conditions. A fully implicit, bi-dimensional, finite volume scheme is applied for the numerical discretization. Variable space and time steps are used to achieve a better precision where the thermal gradients are greater (sample-container interface, container surface). We have modeled 3 cm high, 1 cm diameter Ti+C samples, surrounded by a titanium container of variable thickness. We will present the results obtained with the model for the different experimental conditions, with a special note on the container temperature: too high, and a melting could occur, with a disintegration of the container

(and a titanium-rich layer on the sample surface), too low, and the mechanical properties of titanium will prevent the densification, which is our next expected step.

Comparison between experimental and calculated results is finally performed. It is demonstrated that experimental and calculated results are in good quantitative agreement for the thinner container. For the thicker one, experimental results are in good qualitative agreement and work is in progress to analyze more quantitatively the obtained results.

#### **P-2-172: TiNi Shape Memory Alloy Made by SHS**

*Zhineng Guo, Cunjing Chen, Shiqing Sun, Sheng Yin*

*Department of Powder Metallurgy, University of Science and Technology Beijing  
Beijing 100083, China*

TiNi shape memory alloy (SMA) porosint, a promising artificial bone material, is prepared by self-propagating high-temperature synthesis (SHS). It is found that TiNi SMA porosint can be produced using both propagating and thermal explosion mode in SHS process. The morphology of bores and phase composition were characterized by SEM and XRD. In addition, the temperature of phase transformation of SMA prepared by self-propagating high-temperature synthesis -  $A_s$  was measured. It is found that the key parameters affecting the porosity, the shape and the distribution of bores in the synthesized product are the pre-heating temperature of Ti-Ni compact and the compact density in propagating mode during SHS. TiNi SMA porosint with homogeneously distributed bores can be obtained by igniting the loose Ti-Ni powder through pre-heating at the range of 350°C~400°C. In short, self-propagating high-temperature synthesis is an ideal method for producing TiNi SMA.

**KEY WORDS:** SHS, TiNi shape memory alloy porosint (TiNi SMA porosint), open porosity, phase transformation, temperature

#### **P-1-223: SHS Reactive Joining**

*U. Admon<sup>1</sup>, N. Frage<sup>2</sup> and M.P. Dariel<sup>2</sup>*

*<sup>1</sup> NRCN, PoBox 9001, Beer-Sheva, Israel*

*<sup>2</sup> Department of Materials Engineering, Ben-Gurion University of the Negev  
Beer-Sheva, Israel*

The SHS approach is an innovative and, in the absence of conventional energy sources, the only viable solution for joining metal parts. Two different experimental techniques were investigated. According to the first approach, a 25  $\mu\text{m}$  thick coating, consisting of 500 individual, 50 nm thick NiTi layers, was deposited on Al substrates. Two such coated Al-surfaces, with an intercalated, free-standing 0.1 mm-thick similar Ni-Ti multilayer stack, were joined by spark-ignition the multilayers. The resulting bonding layer consisted of a  $\text{Al}_3\text{Ni}_2$  interlayer that was determined by the initial thickness of the individual Al and Ni layers. According to a second approach, Ti-B-Al powder mixtures were compacted into 5 to 8 mm high pastilles. Graded composition configurations were produced by varying the Al-to-(Ti,B) powder ratio along the axis of the pastilles. The pastilles were placed between Al surfaces and ignited with simultaneous application of axial pressure. The molten Al within the  $\text{TiB}_2$  product of the SHS reaction, formed the solid joint between the Al parts. The effect of various parameters of the graded configuration and of the method of ignition on the strength of the solid joint will be presented.

#### **P-1-108: Percolation Combustion: Is It Possible in SHS?**

*O.S. Rabinovich<sup>1</sup>, B.B. Khina<sup>2</sup>, P.S. Grinchuk<sup>1</sup>, A.V. Belyaev<sup>3</sup>*

*<sup>1</sup>A.V. Luikov Heat and Mass Transfer Institute, National Academy of Sciences of Belarus*

*P. Brovka Str., 15, Minsk, 220072, Republic Belarus*

*<sup>2</sup>Physico-Technical Institute, National Academy of Sciences of Belarus*

*<sup>3</sup>Powder Metallurgy Research Institute with Pilot Plant, Minsk, Belarus*

In situations when the characteristic scales of the SHS front (the sizes of the fast reaction and

preheat zones) are comparable with the sizes structural elements of the reacting system (particle diameter, foil thickness, etc.), propagation of the combustion front demonstrates the alternation of bright flashes and depressions. If the charge has a random structure, roughening of the SHS wave front and transition to scintillating regime are observed [1,2]. The present work is intended to give an answer to the question, “under which conditions the propagation of the SHS process can occur in the percolation regime, i.e., in the form of subsequent ignition of randomly distributed combustible particles constituting an infinite percolation cluster?” Numerical estimations have shown that such regime is possible when each particles burns in the layer-by-layer regime, i.e. when  $x_*$  is a characteristic scale of the reaction zone,  $d$  the particle size. In the opposite case the ignition of a combustible particle by an adjacent burning particle is impossible because of heat losses to the inert environment.

Gasless combustion of simplest 1D and 2D systems is considered where the particles are arranged in the nodes of a regular lattice, the fuel content of the particle being a random value. Mechanically activated powder mixtures used for the SHS of intermetallic compounds (e.g., Ni-Al, Ni-Ti, etc.) are the prototypes of such model systems. The starting powder particles are agglomerates composed of interlaced laminas of two metals [3]. It is well known that during mechanical activation the contact surface area increases by the factor of  $10^4$  to  $10^7$ . Thus, simple estimations demonstrate that such a composite particle can burn in the layer-by-layer regime. Unlike the existing models of random-media combustion [4], the developed approach treats each particle as a macroscopic object with its own nonstationary temperature and concentration fields.

The following results have been obtained by computer modeling:

- at  $x_*/d < 1$  the average combustion wave propagation velocity in a heterogeneous system composed of similar composite particles with the same fuel content considerably exceeds the combustion velocity in a homogeneous system having the same kinetic parameters, fuel concentration and volume-averaged thermal conductivity factor;
- the combustion velocity in a 1D heterogeneous system with random distribution of the fuel concentration in the particles, the average dimensionless fuel concentration being  $\bar{\rho} = 1$ , appears to be higher than the combustion velocity of a similar heterogeneous system composed of particles with equal fuel concentration  $\bar{\rho} = 1$ ;
- with decreasing the ratio  $x_*/d$ , the ratio of the combustion-velocity dispersion to the average velocity increases.

For 2D heterogeneous random systems, the features of the changeover from frontal regimes of the SHS wave propagation to the percolation regime are investigated.

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#### P-2-152: Frontal Polymerization Caused by Centrifugal Field

*V. Briskman, K. Kostarev, A. Shmyrov*

*Institute of Continuous Media Mechanics, RAS, Akad. Korolev Street, 1 Perm 614013*

*Russia, E-mail: [vab@icmm.ru](mailto:vab@icmm.ru); Fax: +7-3422-336957*

Earlier investigations on polymerization of liquid monomers revealed high gravitational sensitivity of this process [1]. It has been found that the intensity of gravitational effect depends on the stage of reaction at which the level of gravity changes. This finding can be treated as a supporting

evidence for the existence of several independent mechanisms of gravitational effect on polymerization and structure formation of polymers. Furthermore, it favors the view that artificial "high gravity" can be effectively used as a means for enhancing and studying separate mechanisms such as sedimentation and convection. Sedimentation of polymer microparticles (polymer nuclei) generated at earlier stages of process occurs until the particles come into contact with each other and loose the ability to move independently. Thermal and concentrational (conversional) convection due to the reaction exothermicity and conversion of a monomer to a denser polymer phase develops at the stage when the reaction mixture behaves itself as a homogeneous liquid.

To gain inside into the nature of gel structuring an experimental setup was designed allowing visualization of the flow and conversion field during polymerization on a centrifuge. The polymerization proceeded in a reactor shaped as a hollow disc which rotated about its axis with a frequency of order of 25 revolutions per second and higher. Observations and interferometric measurements made with the developed experimental setup revealed a new phenomenon due to an increasing a role of sedimentation.

This phenomenon is associated with the formation of gelation front during volumetric reaction or complication of the process during photoinitiated reaction in centrifugal field. The reason is that an acceleration of the gel microparticles sedimentation leads to an increase of their concentration with the increase of a distance from the rotational axis of the reactor. This fact explains why the inhomogeneous conversion field is generated even in thermally initiated reactions with the initiator distributed uniformly throughout the monomer. Under these conditions the formation of gel macrostructure (gel sponge) begins at the reactor periphery, i.e. proceeds in a frontal manner practically independent of the type of reaction initiation.

As the mass of the gel grows the total heat release increases and the front becomes unstable. As a result a convective motion arises in a liquid mixture such that the time of initiation and the form of the motion are defined by the rotation frequency, the size of the reactor and the type of initiation. The measurements of the optical and mechanical properties show that the final structure of the gel samples preserves all specific features of gel formation.

From the results of experiments it may be concluded that high-gravity holds much promise for manufacturing polymer materials with prescribed structure and properties.

The work was supported by the RFBR-"Ural" project 01-03-96487.

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#### **P-1-109: A "Micrometallurgical" Model of Phase and Structure Formation in SHS**

*B.B. Khina<sup>1</sup>, O.S. Rabinovich<sup>2</sup>, B. Formanek<sup>3</sup>, A.V. Belyaev<sup>4</sup>*

*<sup>1</sup>Physico-Technical Institute, National Academy of Sciences,*

*10 Kuprevicha St., Minsk 220141, Belarus. E-mail: khina@cz.itmo.by*

*<sup>2</sup>A.V.Luikov Heat & Mass Transfer Institute, National Academy of Sciences, Minsk, Belarus*

*<sup>3</sup>Silesian University of Technology, Katowice, Poland*

*<sup>4</sup>Powder Metallurgy Research Institute with Pilot Plant, Minsk, Belarus*

Recent studies of SHS waves using microscopic high-speed video recording, which have revealed new patterns of the wave propagation, *viz.*, the relay-race, scintillating and quasi-homogeneous regimes [1], suggest that, along with local inhomogeneity of heat transfer, the interaction mechanisms may be responsible for the origin and changeover of particular regimes.

This necessitates a new insight into the phase formation mechanisms operating in the SHS wave, which due to features (high heating rate, steep temperature gradient and fast accomplishment of reactions) intrinsic in SHS differ substantially from those pertaining to the traditional "furnace" synthesis. Experimental researches [2,3 *et al.*] have shown that melting and spreading is essential in

SHS and the final product is formed by the melt crystallization. However, this phenomena has not been yet included in the models of SHS. The existing models employ a semi-empirical equation for the reaction rate [4],  $\partial\eta/\partial t = (1-\eta)^n \exp(-m\eta) \cdot k \cdot \exp[-E/(RT)]$ , or are based on the concept of quasi-equilibrium diffusion-limited product formation [5]. Within the latter approach [6], melting of a metallic reactant changes the concentrations of diffusing species at the phase boundaries and the diffusion coefficient in the metal phase but doesn't alter the geometry of the elementary diffusion couple wherein the interaction is still limited by a low diffusion rate through the refractory product layer (e.g., TiC). Numerical estimates demonstrate that this mechanism is valid for fine-sized initial metal particles and seems to be pertinent to reactive sintering.

In this work, a new "micrometallurgical" model of phase and structure formation during SHS is proposed. In the preheat zone, solid-state diffusion-limited interaction of the reactants results in the growth of a thin layer of a refractory product on the surface of metal particles. In the zone of thermal reaction, melting of the metal particles occurs. Because of the volume change, the molten metal disrupts the core of the primary product and comes into direct contact with a non-metallic reactant which dissolves in the melt. The grains of the final product crystallize from the melt, which brings about the major heat release responsible for the SHS wave propagation. The crystallization process accomplishes in the after-burn zone.

The model includes heat transfer equation, the equation for the diffusion-limited growth of the primary product and the crystallization kinetics of the final product based on the Kolmogorov-Avrami approach.

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**P-1-90: Non-Steady-State Modes of Filtration Combustion**

*V.V. Grachev*

*Institute of Structural MacrokINETics and Materials Science,  
Russian Academy of Sciences, Chernogolovka, 142432 Russia*

It is well known that the combustion wave propagation may proceed in stable (steady-state) or unstable (non-steady-state) mode. The present study was intended to provide new data on unstable modes of gas-solid system combustion. A layer of green mixture (solid reagent and diluent) in the atmosphere of gas reagent was considered. Heat/mass transfer during filtration combustion was described by using a two-dimensional system of equations. Numerical calculations were performed for the first-order reactions with respect to degree of conversion and zero-order reactions with respect to pressure. Two cases were analyzed without and with heat/mass exchange with environment through the side surface. In the former case, there are only layer-by-layer (or laminar) combustion modes, which are described on the basis of one-dimensional model. In the later case, there are possible both layer-by-layer and surface combustion modes, which are essentially two-dimensional. For the same selected values of system parameters numerical calculations were performed for both cases, and comparison of obtained results were made.

It is shown that the region of existence for two-dimensional unstable modes is wider than for one-dimensional ones, i.e. there exist the region of system parameters values within which the one-dimensional modes are stable whereas two-dimensional modes are unstable (oscillating).

This work is supported by Russian Foundation for Basic Research, grant RFBR 00-15-99054.

**P-1-226: Reaction Retardation and Intensification Waves at the Surface of Gaseless Combustion Front under Heat Losses**

*B.L. Kopeliovich*

*A.V. Luikov Heat and Mass Transfer Institute*

*National Academy of Sciences of Belarus, 220072 Minsk*

The heat losses with gaseless combustion of a mixture in a semi-infinite cylindrical envelope rise owing to decrease in inner radius of the envelope. As a result, the solution of the system of conjugated heat conduction equations for mixture and envelope shows that the character of cyclical changes in combustion wave varies. The reaction retardation wave, appeared at the surface of combustion front, reflects from the sample axis, reaches the front bend near the envelope and becomes steeper. Ahead of the retardation wave arises a region of high chemical reaction rate, where the bifurcation of numerical solution takes place. One branch presents the wave of reaction intensification that trends to the sample axis and increases the activity of chemical sources. The second branch refers to the secondary reaction retardation wave. This wave becomes steeper on the front bend and creates ahead of itself a region of high chemical reaction rate that contracts gradually into a reaction spot. The spot decays after a time and appears again in the next cycle.

The changes in the front surface are accompanied by the changes in the temperature field of combustion wave when the region of highly heated products travels periodically from the sample center to the periphery of the inner range and back.

**Key words:** surface of combustion front, reaction retardation wave, reaction intensification wave, reaction spot.

**P-2-227: Gasless Combustion of a Mixture in Cylindrical Channel of a Limiting Radius**

*B.L. Kopeliovich*

*A.V. Luikov Heat and Mass Transfer Institute*

*National Academy of Sciences of Belarus, 220072 Minsk*

As a result of successive narrowing of cylindrical channel its inner radius takes the limiting value at which the mixture combustion is still possible. The surface of combustion front is flexed in the cup form. The reaction retardation wave arising at the front surface reflects from the sample axis and creates a region of high values of chemical reaction rate directly ahead. At the localization place of this region appears a prominence of the front surface whose size is comparable to the width of a low temperature thermal wave. The axial velocity component of the retardation wave, which slows the motion in radial direction, increases with formation of the prominence without appearance of the angular velocity component. Thus, the combustion process in a sample of the limiting radius holds the axial symmetry.

Two maxima of a chemical reaction rate that move in opposite directions arise as a result of bifurcation of numerical solution. One of them generates a reaction spot at the sample axis, and the other forms a reaction spot near the envelope. A luminous girdle appears and vanishes periodically at a side surface of the sample with merging reaction spots from all the radial sections.

**Key words:** limiting radius of a sample, reaction spot at a sample axis, luminous girdle at the side surface.

**P-2-228: The Induction-Assisted Chemical Oven Technology Applied to the Nitridation of  $\beta$ - $Ti_{63}Nb_{37}$ .**

*A. Martinelli, M. Ferretti*

*Dipartimento di Chimica e Chimica Industriale, Via Dodecaneso 31 – 16146, Genova, Italy*

Several  $\beta$ - $Ti_{63}Nb_{37}$  plates were nitrided thanks to the energy released during the combustion of Nb powders in a nitrogen atmosphere. The reaction were carried out in the reaction chamber of a high temperature-high pressure autoclave and ignited by means of a Cu-coil connected to a high-power

generator. Nitridation was performed in the pressure range 25 – 400 bar. In this paper we compare the properties and the microstructures of samples nitrided applying the traditional combustion technique (i.e. after ignition the high-power generator is turned off) and a new technique that we called induction-assisted combustion that consists in turning off the high-power generator only after few seconds from the ignition of the reaction. In particular in our experiments we turned off the generator after 5 seconds after ignition. In both cases thick layer composed of  $\delta$ -(Ti,Nb)N solid solution were obtained in a time of a few seconds. The region of the solid solution near to the gas/solid interface is characterised by a very high Nb content. The samples nitrided applying traditional combustion show a not-homogeneous microstructure inside which the transition from the external to the internal nitridation regime can be observed. The samples nitrided applying the energy assisted combustion show a homogeneous nitridation, dominated by the growth of an external scale; internal nitridation is confined to grain boundaries.

Samples nitrided by means of the induction assisted technique are characterised by a higher superconductive transition temperature, compared to samples nitrided by means of the traditional technique in the same pressure conditions.

#### **P-1-229: Combustion of Vanadium-Carbon Powder Mixtures at low O<sub>2</sub> pressure**

*A. Martinelli\*, M. Ferretti*

*INFM & Dipartimento di Chimica e Chimica Industriale, via Dodecaneso 31, I-16146 Genova, Italy*

The combustion of vanadium – carbon powders mixtures at low O<sub>2</sub> pressure was studied. The reaction was ignited by means of induction heating; a wave-front was observed propagating throughout the reactants. The combustion temperature,  $T_c$ , is higher than the melting point of V and metal particles melt and coalesce during combustion. The analysis of the so obtained products shows the formation of the two isostructural compounds  $\delta$ -VO<sub>1-x</sub> and  $\delta$ -VC<sub>1-x</sub>, characterised by a fcc structure. The reaction that lead to the formation of the carbide is sustained by the reaction between V and O.

**Key words:** Vanadium carbide; Vanadium oxide; Gas-solid reactions; Microstructures

\* Corresponding author: amartin@chimica.unige.it

#### **P-2-230: Fabrication of TiC-(Al,Ni) Cermets by Reaction Assisted Infiltration**

*H. Prigozin, N. Frage*

*Department of Material Engineering, Ben Gurion University of the Negev, Beer-Sheva, Israel*

Cermets are heterogeneous materials containing both ceramic and metallic phases and are widely used in applications in which high strength and toughness are needed. TiC based cermets with an intermetallic matrix (Ni<sub>3</sub>Al or Al<sub>3</sub>Ni) are known for their physical properties and wear resistance at elevated temperatures. The fabrication of such cermets by free infiltration with a liquid intermetallic phase requires temperatures above 1350°C. The aim of the present work was to determine ways for reducing the fabrication temperature by reaction-assisted infiltration. The preforms for infiltration were compacted from TiC and Ni powder mixtures (10, 15, 20 wt.% Ni) and sintered to different relative densities. The sintered preforms were infiltrated with liquid Al at 1150-1200°C under vacuum 10<sup>-4</sup> torr. The interaction between the Ni particles and liquid Al leads to the intermetallic phase formation in the course of the infiltration stage. The ceramic-to-metal ratio in the resulting composites was calculated on the basis of the initial porosity of the preforms and the desired preform composition. Several cermets with different compositions were fabricated and characterized. For example, infiltration of the preform (20 wt.% Ni) with 30 % porosity with liquid Al leads to the production of a TiC-Al<sub>3</sub>Ni composite with homogeneous structure and a relatively high (about 1250HV) hardness. Infiltration of the preforms, with 40% porosity leads to the formation of cermets with a matrix consisting of Al<sub>3</sub>Ni and excess Al. The hardness of such

composites is about 1000HV. The mechanical properties of the cermets of various compositions will be discussed and related to their microstructure.

**P-1-221: Computer-Aided Analysis of Microstructure of SHS-derived Ceramic Composites**

*G. Górný, M. Raćzka and L. Stobierski,*

*University of Mining and Metallurgy, Department of Advanced Ceramics,*

*30-059 Cracow, al. Mickiewicza 30, Poland*

The paper presents the results of the computer-aided quantitative analysis of microstructure of SHS-derived AlN-TiB<sub>2</sub> composite. Quantitative description of AlN-TiB<sub>2</sub> microstructure parameters and measurement of mechanical properties have been carried out to find the reasons for the observed modification of properties. The investigation of inhomogeneity of TiB<sub>2</sub> particles distribution by systematic scanning method will be presented.

**Key words:** ceramic composite, SHS method, quantitative analysis of microstructure, mechanical properties

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**ISRAELI SECTION OF THE COMBUSTION INSTITUTE**

**RUSSIAN SECTION OF THE COMBUSTION INSTITUTE**

**JOINT ISRAELI-RUSSIAN WORKSHOP ON COMBUSTION**

**February 19, 2002**

**Technion-Israel Institute of Technology, Haifa, Israel**

**Supported by the Technion-Israel Institute of Technology**

## **PREFACE**

This is the first time that such a Joint Israeli-Russian Combustion Workshop takes place, with the support of the Combustion Associations of both countries. We hope that other Workshops will follow.

We are very pleased that, despite the difficult times that we have been facing and the resulting delays, we can now welcome all the participants from abroad and from Israel at our Technion Campus. We are confident that you'll take advantage of being here to enjoy the Technion, the city of Haifa, and Israel.

The Workshop includes articles on different aspects of combustion, presented by scientists and experts. It is a great opportunity for scientists from Israel and Russia along with scientists from the International Community to discuss topics of mutual interest, and to figure out subjects for future collaboration.

Conducting the Workshop within the framework of the VI International Symposium on Self-Propagating High-Temperature Synthesis (SHS-2001) enhances the overall interest and scientific opportunities.

I'd like to take this opportunity to acknowledge the support of Technion in conducting this Workshop.

Once again, I welcome you all and I look forward to a fruitful and enjoyable meeting.

Alon Gany  
Chairman of the  
Local Organizing Committee

## **Session Time-Table**

**19 February, 2002**

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**10:30-10:50 Coffee-break**

**CW-2. 10:50-11:50 Solid Fuel Combustion**

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**CW-3. 12:00-13:00 Energetic Systems**

**13:00-15:20 Lunch**

**CW-4. 15:20-16:40 Combustion Systems**

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## **IRCW-01: NEW DEVELOPMENTS IN DEFLAGRATION-TO-DETONATION TRANSITION RESEARCH**

L. Kagan and G. Sivashinsky

School of Mathematical Sciences, Sackler Faculty of Exact Sciences,  
Tel Aviv University, Tel Aviv 69978, Israel

An identification of the basic mechanisms controlling deflagration-to-detonation transition (DDT) remains one of the major challenges of combustion theory. Recently in the course of studying one-dimensional models of confined combustion it was realized that the transition may well be triggered by the pressure and temperature build-up induced by the system's hydraulic resistance. The nature of the results obtained (the explosive character of the transition, the velocity and pressure overshoots, the predetonational expansion and shrinking of the reaction zone (all these effects are well known experimentally) gives grounds for the belief that in some average sense the actual DDT physics is captured quite adequately.

In the found DDT mode the localized explosion preceding the transition occurs precisely at the flame front. Such transitions are indeed feasible and well documented experimentally. Yet, there are numerous situations where the explosion occurs somewhat ahead of the advancing flame. This salient aspect of DDT, however, seems to be beyond the scope of the one-dimensional approach and calls for further research. The 'remote' initiation, as has long been argued is most likely a product of the predetonational acceleration of the advancing flame, which is virtually absent in the one-dimensional description ignoring the continuous growth of the flame area.

It is therefore desirable to invoke the spatial picture of the phenomenon where the hydraulic resistance is determined directly by the boundary conditions rather than through the effective drag force. The current study reports the first results obtained along these lines.

The two-dimensional formulation reproduces the formation of the so-called tulip flame and its predetonational acceleration, well-known experimentally but unattainable within the one-dimensional approach. It is shown that the detonation first develops in the boundary layer where the effect of hydraulic resistance is stronger, and thereupon spreads over the channel's interior. The second stage of the transition, however, does not proceed gradually but rather through a localized auto-ignition within the tulip. At the moment of its inception the secondary detonation appears to be partially detached from the tulip's base, thus yielding a short-term deflagration-detonation coexistence.

## **IRCW-02: SPINNING DEFLAGRATION AND DETONATION KINEMATICS**

E.N. Rumanov

Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences,  
142432 Chernogolovka, Moscow Region, Russia

Spinning deflagration and detonation have the common origin, enthalpy excess ahead the reaction zone. For deflagration, the smallness of diffusivity is necessary to obtain the spinning regimes while the detonation wave has always the enthalpy excess in its induction zone (between the shock front and the reaction zone). In frame of reference moving with mean velocity along the sample (or the pipe), the spinning wave looks as the rotating spiral of Wiener and Rosenblueth. We discuss the experimental results in the SHS, the gaseous mixture combustion, and the frontal polymerization.

## **IRCW-03: ON MAXIMUM SELF-HEATING UNDER CRITICAL CONDITIONS OF THERMAL EXPLOSION: THEORY AND EXPERIMENT**

A.S. Shtenberg

Semenov Institute of Chemical Physics, Russian Academy of Sciences, Moscow 117977,  
Russia

Methods of the classical thermal explosion theory are used to consider a change in the value of a substance's self-heating as it approaches critical conditions. The analytical expression  $x=y - \ln(y) - 1$  is obtained, connecting unlimited self-heating  $y = \Delta T / \Delta T^*$  with unlimited value  $x = (T_0^* - T_0) / \Delta T^*$ —the difference between external temperature  $T_0$  and its critical value  $T_0^*$ .

It is demonstrated that the value of maximum self-heating  $\Delta T_{\max}$ , approximating to the theoretical value  $\Delta T^* = R(T_0^*)^2/E$ , is rarely realized in practice as a result of great nonlinearity of this dependence. In the experiments designed to measure the critical temperature  $T_0^*$  with precision ( $\pm 0.5 \div 1.0^\circ$ ), standard for such experiments, the most repeatable value of maximum self-heating is  $\Delta T_{\max} \approx 0.7 \Delta T^*$ . Therefore, the values of activation energy  $E$ , calculated on the basis of data from the above-mentioned experiments using a theoretical formula, turn out to be nearly 30% higher than the true value. Analysis of experimental data from the thermal explosion of dinitrodiethylnitramine (dina) confirms the theoretical conclusions of this work.

## **IRCW-04: MICRO-HETEROGENEOUS MECHANISM OF GASLESS COMBUSTION: COMPARISON OF COMPUTER SIMULATION AND EXPERIMENTAL DATA**

A.S. Rogachev

Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences,  
142432 Chernogolovka, Moscow Region, Russia

Macroscopic behavior of combustion wave propagating by micro-heterogeneous (relay-race) mechanism is analyzed. Mathematical model of the process is based on the assumption that reaction medium consists of elemental reaction cells, and heat dissipation within each cell occurs much faster than heat exchange between neighborhoods cells. Utilizing method of computer simulation, dependences of combustion velocity on the initial temperature, rate of heat release, kinetics of chemical reaction is calculated, as well as boundaries between stable and oscillating combustion, and between micro-heterogeneous and quasi-homogeneous regimes. Various kinetic laws, including simple zero-order reaction with Arrhenius temperature dependence and influence of sharp increasing of the reaction rate in the point of phase transformation are considered. The results of calculations are compared with experimental data and quasi-homogeneous theories. The comparison leads to the conclusion that combustion wave propagation in the most gasless systems occurs through micro-heterogeneous mechanism.

This work is supported by RFBR grants 00-15-97370 and 99-03-32392.

## **IRCW-05: A NEW LOOK INTO THE PYROLYSIS AND OXIDATION OF THERMOPLASTICS**

Ezra Bar-Ziv

Department of Mechanical Engineering and Institutes for Applied Research  
Ben-Gurion University of the Negev  
P.O.Box 653, Beer-Sheva, Israel

A new method for the investigation of the pyrolysis and oxidation of thermoplastics has been developed. In this method these processes are studied using a single particle suspended in an electric field. The particle is heated by radiation to the desired temperature and its surroundings can be controlled. The high heating rate ( $10^4$ - $10^5$  K/s) and small size of the particle (50-200 $\mu$ m) prevent mass and heat transfer limitations, inevitable in other methods. The main advantage of this method is that kinetic interpretation is straightforward and unique because chemical reactions are not coupled with heat and mass transfer processes. Due to the fast heating the initial structure of the polymer is not being modified and therefore the results relate to the initial chemical structure and intrinsic rate. In the experiment the following properties were determined in real time: mass, diameter, density, optical properties, and temperature.

The method has been used for investigation of the pyrolysis and oxidation of polystyrene particles. The temperature range investigated was 500-1000K, covering depolymerization and charring mechanisms.

From mass loss rate vs. inverse temperature activation energies were obtained. From mass and diameter measurements density was determined. Density transients have shown the transition from the non-charring to the charring stage.

The novelty of this study is the ability to determine the absorption coefficient of the particle (from the photophoretic force measured in this study). This enabled one to look into the condensed phase during reaction. Since absorption coefficient is related to the extent of cross-linking, direct conclusions on the evolution of the chemical structure of polystyrene has been gained.

## **IRCW-06: UNSTEADY FILTRATION COMBUSTION IN MOVING POROUS MEDIA**

K.G.Shudinsky, G.V.Shudinskaya<sup>1</sup>, B.J.Matkowsky<sup>2</sup>

<sup>1)</sup>Institute of Problems of Chemical Physics, Russian Academy of Sciences, 142432 Chernogolovka, Russia.

<sup>2)</sup>Department of Engineering Sciences and Applied Mathematics, Northwestern University, Evanston, IL 60208, USA.

Filtration combustion describes exothermic chemical conversion waves in porous media by the filtration transport of fluids through the pores of the medium to the reaction zone where it reacts with the solid reactive components of the porous matrix. If the characteristic filtration length is much greater than the preheat length, the wave can be described as quasi-steady, in which the combustion characteristics vary slowly. A general description of quasi-steady filtration combustion waves in immovable media is given in [1-3]. The existence of both one and two stationary reaction zone structures of the filtration combustion front in moving media were studied in [4].

In the present study, we will consider the unsteady filtration combustion in moving porous media. We consider filtration combustion in vertical reactor being fed from above by solid

particles, which move through the reactor with constant velocity. The mixture is ignited from below, and the products of combustion are removed from the bottom of the reactor at the same velocity. We consider a one-dimensional mathematical model and investigate problem of the stability of the filtration combustion waves. If a stationary combustion front is unstable we analyze the new nonstationary periodic regimes of filtration combustion.

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### IRCW-07: INTERNAL BALLISTICS OF A DIVIDED COMBUSTION CHAMBER

E. Sher<sup>1</sup>, M. Arogeti<sup>1</sup>, and M. Lifshitz<sup>2</sup>

<sup>1</sup>Department of Mechanical Engineering

Ben-Gurion University, Israel

<sup>2</sup>IMI, Israel

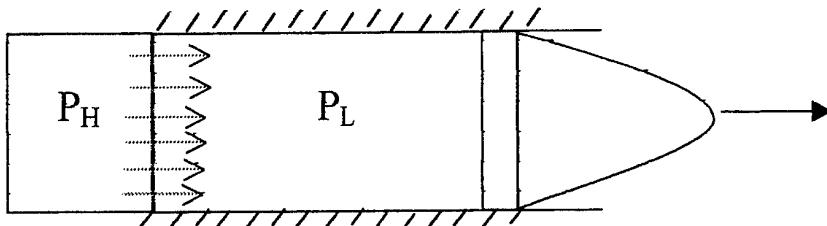
In a conventional gun, the conversion efficiency of the energy stored in the solid propellant into the kinetic energy of the projectile is quite low. This is attributed to the characteristic pressure-time curve in the bore, associated with the combustion process of the propellant. In order to achieve maximal conversion efficiency, the pressure behind the projectile has to be constant, while the energy of the exhausted gases, when the projectile leave the gun, vanishes to zero. Many attempts have been conducted in the past in order to improve the characteristic curve of the bore pressure by controlling the rate of the propellant burning rate. Re-shaping the geometry of the propellants particles is one of the more effective methods. In this way, the time variation of the total surface area of the particles during combustion may be controlled to perform a pre-required behavior.

The present work studies those cases in which low pressure is required to allow lighter and smaller guns. Low-pressure combustion involves problems associated with slow increase in the chamber pressure, in homogeneity in the combustion chamber, and low combustion efficiencies. Using a divided combustion chamber is an interesting attempt to design low-pressure guns. In this type of arrangements, a perforated membrane divides the combustion chamber into two compartments. The back combustion compartment contains the propellant particles, wherein combustion occurs under high-pressure conditions. The partition membrane and the projectile confine the front combustion compartment. This compartment, the low-pressure chamber, is subjected to inflow of hot gases that constitutes the hot products of combustion of the back combustion chamber.

In the present work we study theoretically the effect of some important design parameters of the divided combustion chamber, as well as those of the propellant particles geometry, on the energy conversion efficiency of a given gun (length and bore) and projectile body. The detailed model, model calibration, model verification, and optimization results are presented. The important design parameters are the maximal allowed pressure and the required muzzle

velocity. The design factors to improve the performance are the volumetric ratio between the compartments, the size of the membrane apertures and parameters that define the propellant.

It is shown that for a specific gun design a divided chamber gun is more efficient, than an undivided chamber gun, the ballistic efficiency is higher, e.g., the required muzzle velocity is achieved with a lower amount of propellant. An optimal ratio between the two chamber volumes has been found. Very small volumes of the high-pressure chamber result in a sharp decrease of the ballistic efficiency. However the volume is restricted by the maximum allowed loading density (the ratio between the propellant mass and the chamber volume). When the aspect ratio (the ratio between the aperture area and the cross-section of the barrel) increases, the efficiency of the ballistic cycle approaches that of an undivided chamber gun. For an aspect ratio above 5%, the efficiencies are practically identical. It was concluded that there is an optimal area aspect ratio for a maximum efficiency for any required maximal allowed pressure.



The divided combustion chamber: The high pressure and low pressure compartments are divided by a perforated membrane

## IRCW-08: THERMODYNAMIC BLOCKING OF BORON COMBUSTION

Alon Gany

Faculty of Aerospace Engineering

Technion-Israel Institute of Technology, Haifa 32000, Israel

Boron exhibits remarkable theoretical heat of combustion when burning with air: approximately 40% higher than of hydrocarbon (HC) fuels on a gravimetric basis (about 58 vs 44 kJ/g) and some 200% higher on a volumetric basis (about 136 vs 42 kJ/cm<sup>3</sup>; the highest value among all the elements). Hence, the use of boron as a fuel ingredient in air-breathing propulsion seems to be very attractive, particularly for volume-limited systems.

However, in practice, the utilization of the potential combustion energy of boron in actual propulsion systems has often resulted in poor efficiency and low energetic performance.

The objective of this presentation is to highlight a new aspect of boron combustion that might reveal a fundamental physical limitation on obtaining good combustion efficiencies under typical operating conditions of air-breathing combustors.

During the pre-ignition stage, boron particles are coated by a liquid boron oxide layer (melting point 723K), which slows down the reactive interactions between the boron and the surrounding oxygen. As the temperature increases, the evaporation rate of the oxide layer is accelerated. It is believed that at a certain temperature, around 1900-2000K, the evaporation rate exceeds the chemical formation rate of the oxide layer, leading to exposure of the

underlying boron to direct attack of the oxidizing gases. Only then an extensive combustion stage, whose existence has been demonstrated in experiments with individual boron particles, can be established.

The primary claim of this presentation is, that this crucial situation of exposure of the boron to the surrounding gas, namely full evaporation of the oxide layer, which is essential to the establishment of fast boron combustion, may not occur in real systems.

The problem is associated with the concentration of boron and combustion products in the combustion chamber, and thus cannot be observed when testing (or modeling) the combustion of individual particles.

At given operating conditions, evaporation of the liquid boron oxide layer can only take place if the partial pressure of gaseous boron oxide in the surrounding gas lower than the equilibrium vapor pressure of boron oxide at the particle temperature. While this is generally the case when burning individual particles in a stream of air, it may not be case in actual combustors.

Thermochemical equilibrium calculations of combustion products of boron-based fuel combinations with air at ranges and operating conditions typical to solid fuel ramjet combustors have been made. The study consists of the following parameters: a fuel composed of hydroxyl-terminated-polybutadiene (HTPB) and different mass fractions (from 20% to 100%) of boron; fuel/air equivalence ratio between 0.5 and 1; chamber pressure from 0.1 to 2 MPa (14.7 to 300 psia).

The results reveal that for adiabatic combustion of pure boron at stoichiometric fuel/air ratio (equivalence ratio of 1) no liquid boron oxide should exist, hence from the thermodynamic equilibrium standpoint, combustion of boron can take place. However, for lower equivalence ratios (namely, excess air), the partial pressure of the gaseous boron oxide might attain the equilibrium vapor pressure, leading to coexistence of a liquid boron oxide phase. Such a result indicates that some of the liquid boron oxide layer remains on the boron particles. As a consequence, according to the current understanding, this situation might imply the avoidance of establishment of full combustion.

Thus, basic thermodynamic considerations reveal a significant aspect of boron combustion, interpreting an inherent cause for a poor combustion efficiency in actual air-breathing propulsion systems.

## IRCW-09: INSTABILITY AND TRANSVERSE WAVES AT SOLID PROPELLANTS AND EXPLOSIVES

Istratov A.G., Marshakov V.N., Ananiev A.V., Melik-Gaikazov G.V., Puchkov V.M., Smirnov B.N., Sokolovski F.C.

Semenov Institute of Chemical Physics, Russian Academy of Sciences, 4 Kosygin St.,  
Moscow 117977, Russia

We investigated spatial, temporary and temperature heterogeneity caused by spontaneous instability of burning wave in conditions, when the burning as a whole occurs stationary.

Displays of instabilities is revealed experimentally for all investigated substances (double-base and composition propellants, AP, pyroxylin and some explosives, for example hexogen) in all a range of burning conditions (pressure from 1 up to 80 kg/sm<sup>2</sup>, initial temperature up to 70°C). The basic characteristics of unstable burning and laws of their change are determined at change of pressure by means of various techniques (study of the extinguished surface, radiance and electrical conductivity measurements in the burning waves, micro-thermocouple measurements, video filming).

The results are explained from uniform positions within the framework of the offered theoretical model outgoing from representations about cross (transversal) burning waves, similar to spinning burning in SHS.

## IRCW-10: EVOLUTION OF A SPHERICAL SPRAY FLAME

J. B. Greenberg

Faculty of Aerospace Engineering

Technion - Israel Institute of Technology Haifa 32000, Israel

email:

In recent experimental research [1] the propagation of a spherical laminar flame front through a mixture of fuel droplets and air was investigated. It was found that the presence of the droplets was responsible for cellular and pulsating flame fronts that were clearly observed. In view of these findings Near Equidiffusional Flame (NEF) analyses of planar laminar spray flames were carried out [2,3] to try to pinpoint the mechanism responsible for the onset of the observed instabilities. It was shown that heat loss suffered by the system, as a result of the absorption of heat by the droplets for evaporation, triggered the behavior of the spray flame front.

Although it is well known that an NEF analysis is to be preferred when examining the question of flame instabilities, a slowly varying flame (SVF) analysis is more appropriate if a relatively simple evolution equation for the flame front is sought [4].

The question of the ignition of a mist of droplets is of prime importance in the context of the re-light problem in aircraft. Despite this fact there is rather sparse experimental evidence available in the literature (see, for example, [5,6]) and few theoretical works. In the case of the latter, derivation of rules of thumb, based on overall balance of energy considerations, seems to be the general trend [7-9]. In a more detailed numerical model [10] ignition of a polydisperse mist of droplets in a tube, due to heating at one of its ends, was considered. It was shown that, in the configuration that was investigated, the Sauter mean diameter is not suitable for describing the ignition characteristics of a polydisperse spray.

In previous work [11] numerical simulations of a spherical flame front propagating through a mixture of fuel droplets and air were presented. The emphasis was on the complex chemical and thermal structure of the evolving flame so that the operating conditions always ensured the continued existence of the flame front. In the current paper the same problem is examined but the treatment is analytic within the framework of an SVF model. Upon attaining their boiling temperature the droplets are assumed to begin to vaporize, downstream of the propagating flame front, whose location as a function of time is determined as part of the solution. An evolution equation for the flame front is derived. It is shown that the droplets supply a heat loss term in this equation involving the droplet loading and the latent heat of vaporization of the liquid fuel. Unlike the aforementioned numerical research the main aim here is to look into conditions for the possible extinction of the flame front and the way they are influenced by the presence of the spray of droplets.

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### **IRCW-11: SPINNING WAVES IN PRESENCE OF HEAT LOSSES TO ENVIRONMENT OF SOLID CYLINDRICAL SAMPLE**

T. P. Ivleva, and A. G. Merzhanov

Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences,

142432 Chernogolovka, Moscow Region, Russia

We consider gasless combustion with heat losses. If radius of cylinder is big enough, pulsating modes become unstable and reform to spinning modes. Depending on radius size various modes can arise. For non-adiabatic case, the maximum temperature in reaction front can be significantly higher than adiabatic temperature.

The modes obtained in adiabatic case also exist in non-adiabatic case. Although these modes retain their main properties, the front becomes very curved. The spots move along the surface of cylinder to the point of the extinction.

There is non-uniqueness, so the mode can reform to any other mode with less number of spots depending on speed of heat losses increasing. The direction of spot moving can remain the same or become opposite.

It was found that mixture on the surface of cylinder could be unburned. In the spot traces the conversion depth is full, but unburned mixture could be between these traces.

We show that increasing of heat losses leads to increasing of helix step and its angle to horizontal plane.

### **IRCW-12: ENERGY CONCENTRATION IN COMBUSTION WAVES AS A SOLUTION OF PROBLEM FOR LOW CALORIFIC FUEL BURNING**

V.S. Babkin

Institute of Chemical Kinetics and Combustion Russian Academy of Sciences, Novosibirsk  
630090, Russia

Energetically, the concept of sustainable development includes the problems of energy balance, energy-saving, alternative and restored sources. Concerning the chemical natural sources of energy, attention is focused on the efficiency of energy utilization, the use of low-

calorific fuels, a decrease of the level of ecological hazard. Since the low-calorific fuels are often non-burning or difficultly burning, they need special methods of combustion for producing thermal, mechanical or electric energy. One of the novel and promising methods is the method based on the phenomenon of energy concentration in combustion waves. The essence of the method is that in certain conditions, the energy of inner resources of a fuel system in the natural way can accumulate in the combustion zone. This leads to an increase in the reactivity of the reacting medium.

Combustion waves are considered in which the effects of energy concentration, i.e., spiral waves, cellular flames, pulsating and filtration combustion are observed. It is concluded then that the phenomenon of energy concentration in combustion waves is wide spread in nature. The systems, regimes and combustion processes where it is implemented are quite different. The mechanisms of energy concentration also differ from one another. Energy concentration involves both the heat-and mass-exchange processes, gas compressibility, phase transitions, filtration of a mobile phase, and, probably, the other elementary processes.

Energy concentration determines the existence of "exotic" flames (spin or cellular), the flames with unique properties such as "superadiabaticity", the wider parametric areas of flammability and others. The unusual properties and regularities of flames with excess energy are rather promising for combustion of low-calorific fuels. In this case, most attractive are the flames with a convective mechanism of energy concentration implemented in, e.g., certain condition in filtration combustion waves.

There are analyzed the potentialities and schemes of burners and the technologies of the combustion of low-calorific fuels when implementation the flames with excess energy in artificial conditions. Theirs ecological and energetic characteristics, their advantages and disadvantages, principle and technical limitations are discussed.

## **IRCW-13: TURBULENCE- CHEMISTRY INTERACTION CALCULATIONS FOR IMPROVED NO<sub>x</sub> PREDICTIONS**

Yeshayahou Levy and Patric Arfi

Faculty of Aerospace Engineering

Technion-Israel Institute of Technology, Haifa 32000, Israel

e-mail:

NO<sub>x</sub> prediction in combustion systems is highly dependent on the accuracy of the temperature field inside the combustor and on the accuracy of its chemistry modeling. Hence, there is an ever growing demand to improve the physical models that affects the local temperature and concentration.

Turbulence-chemistry interaction affects local temperature, local extinction and hence flame stability. In the present study, the chemical quenching time was calculated using a detailed mechanism for different inlet temperature conditions ( $300 < T_{inlet} < 1800\text{K}$ ) and varying the fuel equivalence ratio (between 0.4 and 1.8). The quenching time is calculated assuming stable combustion, then residence time is decreased and the value just before the time at which the steady PSR solution leads to the sudden temperature drop is chosen as the quenching time. Results of this parametric study show close agreement to the literature.

Thus, the critical residence time of the reactions leading to flame extinction is strongly dependent on the inlet temperature and fuel equivalence ratio. It can be seen that as expected

the chemical quenching time, for a fixed composition, decreases as the inlet temperature is increased. This is especially true far from stoichiometry. The effect of fuel-air ratio can be described by an increase of quenching time with departure from stoichiometry. At high inlet temperatures the effect of fuel air ratio on chemical quenching time is weaker and nearly insignificant for inlet temperatures higher than 1200K. It can therefore be stated that at temperatures above 1200K the chemical quenching time is less sensible to the mixture-air ratio and lie at relatively low values (between 10 and 100  $\mu$ s). This makes such mixture less sensible to strain induced extinction. This remark is important for combustion systems based on combustion at high temperatures of an ultra-lean or rich mixture.

It can be stated that increasing the inlet temperature of the reactants strongly decreases the chemical time scale responsible for extinction and shifts the lowest attainable temperature at steady state combustion to only slightly higher values. The final temperature may be decreased by using lean mixtures without impairing on the chemical quenching time for sufficiently high inlet temperature of the reactants. This dependence is important for combustors based on highly preheated air associated with lean combustion as in the secondary combustion of staged combustion.

To conclude it can be stated that with a higher inlet temperature a lean mixture can be more resistant to local extinction than a flame with low inlet temperature reactants at stoichiometry. In addition the first mixture will allow obtaining lower temperature peaks.

#### **IRCW-14: ABSOLUTE CONCENTRATION AND TEMPERATURE MEASUREMENTS IN FLAMES USING ULTRASENSITIVE ABSORPTION SPECTROSCOPY TECHNIQUES**

N. Ditzian<sup>1</sup>, I. Rahinov<sup>1</sup>, V.A.Lozovsky<sup>1,2</sup>, S.Cheskis<sup>1</sup>

<sup>1)</sup> School of Chemistry, Sackler Faculty of Exact Sciences, Tel Aviv University,  
Ramat Aviv, Tel Aviv 69978, Israel

<sup>2)</sup> Semenov Institute of Chemical Physics, Russian Academy of Sciences, 4 Kosygin St.,  
Moscow 117977, Russia

Absolute concentration measurements of atoms and radicals in flames are very important for a better understanding of combustion mechanisms. Recently, several laser based methods were successfully used for such measurements. Among them are two ultrasensitive methods of absorption spectroscopy: Intracavity Laser Absorption Spectroscopy (ICLAS) and Cavity Ring-Down Spectroscopy (CRDS). This lecture reviews and discusses the current status of the application of these techniques to the absolute concentration and temperature measurements in flames. The principles of these are discussed and comparative advantages and disadvantages are analyzed. We will discuss also recent measurements of absolute concentrations of radicals in hydrocarbon flat premixed flames comparing these measurements with computer simulations.

## **IRCW-15: ACOUSTIC POLLUTION FROM DIFFERENT COMBUSTORS: DIAGNOSTICS AND ACTIVE CONTROL TO SUPPRESS NOISE**

N.I.Kidin<sup>1</sup>, V.V.Afanasiev<sup>2</sup>, S.V. Ilyin<sup>2</sup>

<sup>1</sup>Institute for Problems in Mechanics, Russian Academy of Sciences  
101, bl.1, Prospekt Vernadskogo, Moscow, 117526, Russia

<sup>2</sup>Chuvash State University, Moscovski prospekt 15, Cheboksary, 428015, Russia

Electroacoustic characteristics of various acoustic oscillators operating on the basis of modulated electrical discharges (under unconfined conditions and in the plasma jet channel) are studied. Modulated are both the voltage and current. The acoustic vibration radiation is shown to be due to varying Joule heat release and to subsequent adiabatic expansion of the pulsating plasma jet at the acoustic modulation frequency. The results of experimental studies of acoustic instability in model and real ramjet and liquid rocket combustors are presented in the form of the spectrum of the pressure- oscillation response to harmonic perturbations generated by the modulated discharges. It is shown that the predominant mechanism of the modulated-discharge effect on the combustion zone is variation of the chemical reaction rate induced by intermittent Joule heat release.

A new promising method for active control of unstable combustion modes is developed. The method is essentially based on the use of electrical discharge with the current or voltage-stabilized power source. Both the theoretical estimations and experiments in a model combustor showed that the discharge with a current-stabilized source suppressed the resonant pressure oscillations for all the modes, while with the voltage-stabilized source the pressure oscillations were amplified.

A selective sensitivity of the combustion zone to external perturbations is discovered in experiments with premixed hydrocarbon flames subject to action of modulated discharges, i.e. the amplitude- frequency characteristics of the burning process exhibit resonances. The responses of names of various hydrocarbons premixed with air or oxygen at various initial pressures and temperatures with and without inhibiting additives are studied. The experiments performed in model combustors revealed that combustion instability arises when the fuel resonance coincides with the acoustic combustor resonance.

The developed methods and results are also applicable to propellant combustors and hybrid solid propellant chambers.

The similar approach is developed now for control of deflagration to detonation transition in model combustion tunnels.